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# RESEARCH IN FLUORO-NITRO COMPOUNDS



Contract Nonr-2655(00)
ARPA Order No. 170-61, Project Code 9100

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*Chemical Products Division*

Aerojet-General® CORPORATION

AZUSA, CALIFORNIA THE GENERAL TIRE SACRAMENTO, CALIFORNIA

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

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March 1962

Report No. 0235-01-13
(Quarterly)

# RESEARCH IN FLUORO-NITRO COMPOUNDS

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## ABSTRACT

5,5-Dinitro-2,2-bis(difluoramino)hexane and 5,5,5-trinitro-2,2-bis(difluoramino)pentane were prepared from the corresponding nitroketones and difluoramine in sulfuric acid under pressure.

t-Butyldifluoramine was absorbed by sulfuric acid without gas evolution. Hydrolysis of the intermediate gave acetone quantitatively.

Difluoramine was added for the first time to a simple linear olefin (1-octene).

Preliminary evidence was obtained suggesting the formation of t-butoxydifluoramine from t-butylhydroperoxide and difluoramine.

Ethyl N-fluorocarbamate reacted with aliphatic aldehydes in the presence of a trace of hydrochloric acid to give the corresponding monoadducts and diadducts. Adducts of ethyl N-fluorocarbamate and olefins (octene-1, ethyl vinyl ether, methyl acrylate) were also prepared in the presence of mineral acids.

The reaction of ethyl N-fluorocarbamate with sulfuric acid gave an unstable compound that reacted with n-butyraldehyde to give n-butyronitrile, as would be expected for fluoramine.

Aqueous fluorination of the butyraldehyde - ethyl N-fluorocarbamate diadduct resulted in the replacement of one of the carbethoxy groups by fluorine.

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Report No. 0235-01-13

## I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials of interest for military applications. During this report period work was continued on the alkylation reactions of difluoramine and the aqueous fluorination reaction. A study of the reaction of fluorocarbamates with carbonyl and unsaturated compounds was also initiated.

## II. TECHNICAL DISCUSSION

### A. REACTIONS OF DIFLUORAMINE (K. Baum)

#### 1. Discussion

##### a. Nitroketones

Previous attempts to convert 5,5-dinitro-2-hexanone and 5,5,5-trinitro-2-pentanone to the gem-difluoramines resulted only in the recovery of unchanged starting material.* 5-Nitro-2-hexanone, however, yielded 5-nitro-2,2-bis(difluoramino)-hexane, although a considerable amount of starting material was also recovered.** The sluggishness of this reaction suggested that the polynitroketones might also react with difluoramine under more severe conditions.

Difluoramine reactions have usually been carried out in these laboratories at atmospheric pressure at the reflux temperature of difluoramine over sulfuric acid (-10 to -20°C). With this method, the reaction periods cannot conveniently be extended beyond 6 or 7 hours. In order to prolong the reaction time and also to permit the use of a higher temperature, glass pressure vessels with Fisher-Porter Teflon needle valves were used.

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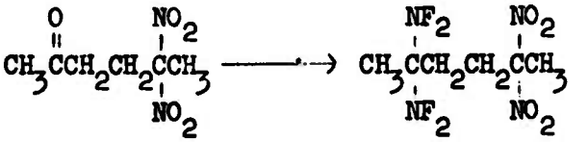
*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 8 (Confidential).

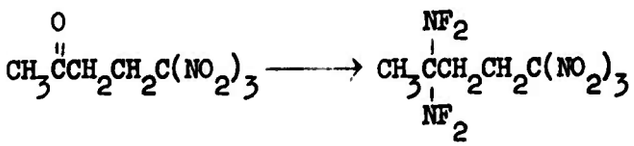
**Aerojet-General Report No. 2099, November 1961, p. 9 (Confidential).

5,5-Dinitro-2-hexanone was thus treated with an excess of difluoramine in 100% sulfuric acid for 20 hours at ambient temperature. A solid product insoluble in the sulfuric acid was formed; this insolubility allowed the convenient isolation of the product by physical separation. In the previous preparation of 5-nitro-2,2-bis(difluoramino)hexane, on the other hand, a tedious column-chromatography purification was necessary because of the similarity of the properties of the starting material and the product. The melting point of the product from the dinitroketone, 47°C, did not change after sublimation. Infrared and nuclear-magnetic-resonance (NMR)* spectra (Figures 1 and 2, respectively) and elemental analysis were used to identify this material as 5,5-dinitro-2,2-bis(difluoramino)hexane:



The quenching of the sulfuric-acid solution with ice resulted in the recovery of 47% of the original starting material. Thus, a longer reaction time is indicated for the optimum yield.

The reaction of 5,5,5-trinitro-2-pentanone with difluoramine was attempted with the same apparatus used for the dinitroketone, and the reaction period was extended to 40 hours. The same course was followed. The product (mp 42°C) also was insoluble in concentrated sulfuric acid. It was identified as 5,5,5-trinitro-2,2-bis(difluoramino)pentane by means of its infrared and NMR spectra (Figures 3 and 4, respectively) and by elemental analysis:



The conversion amounted to 53%, and approximately 10% of the starting material was recovered from the acid layer.

*The NMR spectra are discussed in the sections dealing with experimental results. H. M. Nelson carried out NMR analysis and interpretation.

Impact stability and differential-thermal-analysis (DTA) data for 5,5-dinitro-2,2-bis(difluoramino)hexane and 5,5,5-trinitro-2,2-bis(difluoramino)-pentane are tabulated below.

| | 5,5-Dinitro-2,2-bis(difluoramino)hexane | 5,5,5-Trinitro-2,2-bis(difluoramino)-pentane | RDX |
|---|---|---|---|
| Impact stability, cm/2 kg | | | |
| 100% detonations | 20 | 10 | 40 |
| 50% detonations | 16 | 6.8 | 28 |
| 0% detonation | 14 | 5 | 21 |
| DTA exotherm, °C | 197 | 159 | - |

These compounds are surprisingly stable when it is considered that 5,5,5-trinitro-2,2-bis(difluoramino)pentane is in almost the exact stoichiometric balance for decomposition to CO, HF, $N_2$, and $H_2O$. The melting points are low enough for these materials to merit consideration as plasticizers for propellant formulations utilizing both oxygen and fluorine oxidizers.

b. Olefins

The addition of difluoramine to simple olefins has been accomplished only with examples capable of forming tertiary carbonium ions, such as isobutylene.* Attempts to extend this reaction to unbranched olefins have led only to decomposition. However, reaction at the terminal carbon resulted in the case of conjugated olefins, such as acrylic acid.**

The isobutylene adduct, t-butyldifluoramine, has been reported to be unstable in sulfuric acid, yielding a mixture of acetone and 2-difluoramino-2-propanol.*** The failure to form 2,2-bis(difluoramino)propane in this reaction, despite a large excess of difluoramine, suggested that the

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*Rohm & Haas Company Report P-60-18, 18 November 1960, p. 22 (Confidential).

**Aerojet-General Report 0235-01-11, 14 July 1961, p. 3 (Confidential).

***Aerojet-General Report 2099, November 1961, p. 10 (Confidential).

acetone was not formed in the sulfuric-acid solution, but rather was formed during the subsequent quenching with water.

In order to test this hypothesis, a sample of t-butyldifluoramine was introduced into a bulb containing some sulfuric acid. The pressure in the bulb began to decrease immediately after the t-butyldifluoramine was injected, becoming 8% of the theoretical value for a molar amount of perfect gas in 4 hours, and 5% in 2 days. The quenching of the sulfuric acid with ice then gave a quantitative yield of acetone. Thus, a nonvolatile intermediate is formed in the reaction of t-butyldifluoramine with sulfuric acid, and difluoramine is not liberated.

A plausible intermediate for this reaction is 2-(difluoramino)-2-methyl-1-propanesulfonic acid, which might be formed from the direct sulfonation of t-butyldifluoramine. Isobutylene, formed from the reversal of the difluoramine alkylation reaction, could also be sulfonated, followed by the alkylation of difluoramine:

$$(CH_3)_3CNF_2 \xrightarrow{H_2SO_4} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle NF_2}{\overset{|}{\underset{|}{C}}}} - CH_2SO_3H + H_2O$$

$$(CH_3)_3CNF_2 \rightleftharpoons C(CH_3)_2 = CH_2 + HNF_2$$

$$C(CH_3)_2 = CH_2 \xrightarrow{H_2SO_4} HOC(CH_3)_2CH_2SO_3H$$

$$\rightleftharpoons \oplus C(CH_3)_2CH_2SO_3H \xrightarrow{HNF_2} NF_2\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2SO_3H$$

The hydrolysis of this sulfonic acid would yield methanesulfonic acid, difluoramine, and acetone:

$$NF_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2SO_3H \xrightarrow{H_2O} HNF_2 + (CH_3)_2CO + CH_3SO_3H$$

Sulfonation could also be the cause of the failure to form difluoramine adducts from simple unbranched olefins. An attempt was therefore made to add difluoramine to 1-octene with only a catalytic amount of sulfuric acid; however, the unchanged starting material was recovered. In another attempt, the olefin was added to a refluxing mixture of difluoramine and sulfuric acid, using the standard conditions, with the exception that as soon as the addition was finished, the mixture was poured over ice. In this experiment a 9% yield of difluoraminooctane was isolated, as well as a large amount of viscous, undistillable residue. The difluoraminooctane was identified by means of its infrared spectrum (Figure 5) and elemental analysis. The yield should be improved by a more rapid addition of the olefin to the $HNF_2$-$H_2SO_4$, using cooling. Because the NMR spectrum is not yet available, the direction of addition is not established. It seems reasonable to expect the introduction of the difluoramino group to take place at the secondary position:

$$CH_3(CH_2)_5CH = CH_2 \xrightarrow[H_2SO_4]{HNF_2} CH_3(CH_2)_5\underset{\displaystyle NF_2}{\overset{\displaystyle |}{C}}HCH_3$$

An additional example of the Michael addition of difluoramine to α,β-unsaturated acids was also examined. Thus, the reaction of crotonic acid with difluoramine in sulfuric acid proceeded smoothly to give a 1-to-1 adduct, as shown by elemental analysis. Although the NMR spectrum is not yet available, it can be assumed on the basis of analogous reactions that the difluoramino group entered into the β position:

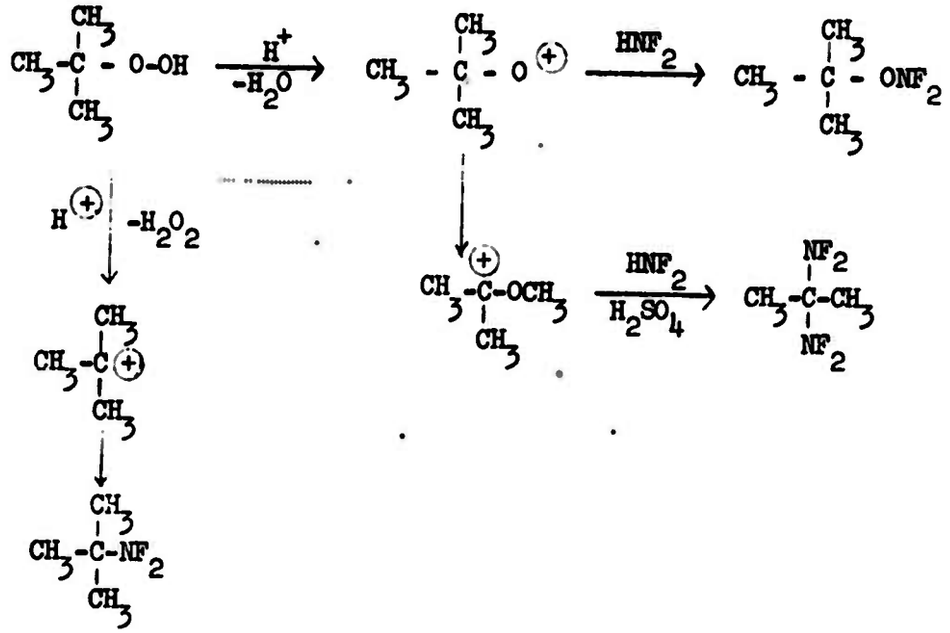
$$CH_3CH = CHCOOH \xrightarrow[H_2SO_4]{HNF_2} CH_3\overset{\displaystyle NF_2}{\overset{\displaystyle |}{C}}HCH_2COOH$$

Figure 6 shows the infrared spectrum of the adduct.

c. Peroxides

Several possible courses can be envisioned for the reaction of alkyl hydroperoxides and dialkyl peroxides with difluoramine in acid. Thus,

t-butylhydroperoxide could be protonated at the hydroxyl oxygen and lose water to form a positive oxygen species. This intermediate might displace a proton from difluoramine to form an O-$NF_2$ compound, or might undergo methyl migration to give an acetone derivative. On the other hand, protonation of the alkyl oxygen and loss of hydrogen peroxide would yield t-butyldifluoramine. These reactions are shown below.



When difluoramine was allowed to reflux over t-butylhydroperoxide in the absence of acid, no evidence of reaction was observed. The dropwise addition of sulfuric acid, however, resulted in a very vigorous reaction, and cooling was required to keep the temperature under control. After an excess of acid had been added, the product was immediately pumped off. The infrared spectrum of this material indicated that it was mainly t-butyldifluoramine.

A similar reaction was carried out using di-t-butylperoxide as the starting material; the volatile product in this case was also t-butyldifluoramine:

$$(CH_3)_3C\text{-}O\text{-}OC(CH_3)_3 \xrightarrow[H_2SO_4]{HNF_2} (CH_3)_3CNF_2$$

The formation of t-butyldifluoramine from t-butylhydroperoxide does not necessarily indicate that the initial heterolysis takes place at the alkyl-oxygen bond. This product might also be formed by an oxygen-oxygen cleavage to form the $ONF_2$ compound, with a subsequent cleavage of the C-O bond of this product to give a carbonium ion. A possible means of reducing or eliminating this degradation is the use of a minimum quantity of acid to catalyze the reaction.

An experiment was therefore carried out in which only one drop of sulfuric acid was added to a mixture of t-butylhydroperoxide and difluoramine. After the exothermic reaction subsided, the excess difluoramine was removed. Two liquid phases remained, one of which appeared to be water. The organic phase was taken up with solvent and its infrared spectrum was determined. There was virtually no starting material or t-butyldifluoramine present, but there were peaks at 5.9, 6.2, 7.3, 7.7, 8.4, 8.7, 10.3, and 11.5 microns. The solvent was distilled from the solution, but the sample fumed off as soon as the solvent was removed.

Although more work is obviously needed before the course of this reaction can be definitely established, the formation of water and the infrared spectrum of the organic product are consistent with the formation of t-butoxydifluoramine:

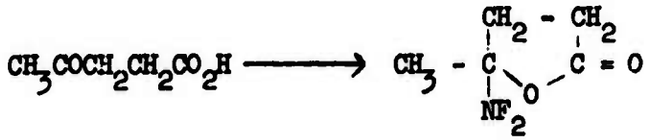
$$(CH_3)_3C\text{-}OOH \xrightarrow[(trace)]{H^+} (CH_3)_3CONF_2 + H_2O$$

d. Miscellaneous Reactions

The reactions of both acetonylacetone and levulinic acid with difluoramine in concentrated sulfuric acid previously gave cyclic products rather than gem-difluoramines:*

$$CH_3COCH_2CH_2COCH_3 \longrightarrow CH_3 - \underset{NF_2}{\overset{CH_2}{C}} \underset{O}{\diagdown\diagup} \underset{NF_2}{\overset{CH_2}{C}} - CH_3$$

*Aerojet-General Report 0235-01-10, 14 April 1961 (Confidential).



The results of the work with nitroketones, however, suggested that, under more drastic conditions, these rings might be opened to form the desired gem-difluoramines. These reactions were therefore repeated in a pressure reactor at ambient temperature, using reaction periods of 44 and 40 hours, respectively. Fuming rather than concentrated sulfuric acid was used. In both cases, however, only the previously obtained heterocyclic products were isolated.

A small amount of additional work was done on the addition of difluoramine to ethoxyacetylene. The products were found to be unstable, decomposing even after storage for 1 day in a refrigerator. In one case a small sample exploded during an attempt at gas chromatography.

The product isolated previously from the reaction of dicyclohexylcarbodiimide* was found to contain no fluorine. No further work was done with this material.

2. Experimental

a. 5,5-Dinitro-2,2-bis(difluoramino)hexane

A solution of 1.9 g (0.01 mole) of 5,5-dinitro-2-hexanone in 40 ml of 100% sulfuric acid was placed in a glass pressure vessel, and approximately 6 g of difluoramine was condensed over this solution. After the mixture was allowed to stand at ambient temperature for 20 hours, the difluoramine was vented off. A solid phase was present above the sulfuric acid; it was separated, dissolved in methylene chloride, washed with water, dried over sodium sulfate, and stripped of solvent. The residue consisted of 0.5 g (0.0018 mole, 18% conversion, 34% yield) of white solid (mp 47°C). An analytical sample was sublimed at 0.1 mm Hg with a 100°C bath.

Anal. Calcd. for $C_6H_{10}N_4F_4O_4$: C, 25.9; H, 3.6; N, 20.1; F, 27.3. Found: C, 26.0; H, 3.47; N, 19.8; F, 26.7.

*Aerojet-General Report 0235-01-12, December 1961, p. 6 (Confidential).

The sulfuric-acid layer was poured over ice and was extracted with methylene chloride to yield 0.90 g (0.0047 mole, 47% recovery) of the starting material.

The proton-NMR spectrum of the product (Figure 2) was obtained in a carbon tetrachloride solution, with tetramethylsilane (TMS) as an internal standard. The higher-field methylene multiplet is nearly obscured by an intense signal at 7.93 ($\tau$ units) that is assigned to $-C(NO_2)_2CH_3$ protons. The spectrum is consistent with the following structure: $CH_3-C(NO_2)_2CH_2CH_2C(NF_2)_2CH_3$.

b. 5,5,5-Trinitro-2,2-bis(difluoramino)pentane

A solution of 2.2 g (0.01 mole) of 5,5,5-trinitro-2-pentanone in 40 ml of 100% sulfuric acid was treated with approximately 6 g of difluoramine at ambient temperature for 40 hours in a pressure reactor. The difluoramine was then vented; the acid-insoluble solid was separated, dissolved in methylene chloride, washed with water, and dried over sodium sulfate. Removal of the solvent left 1.64 g (0.0053 mole, 53% conversion) of white solid (mp 42°C).

Anal. Calcd. for $C_5H_7N_5O_6F_4$: C, 19.4; H, 2.27; N, 22.7; F, 24.6. Found: C, 19.5; H, 2.32; N, 22.6; F, 24.8.

The quenching of the sulfuric-acid layer with ice yielded 0.5 g of an approximately equal mixture of 5,5,5-trinitro-2-pentanone and 5,5,5-trinitro-2,2-bis(difluoramino)pentane, as shown by the infrared spectrum. The proton-NMR spectrum of the product (Figure 4) was obtained in carbon tetrachloride solution, with TMS as an internal reference. The terminal-methyl-group signal appears at 8.29 ($\tau$ value). It is split into a quintet by the two $-NF_2$ groups on the adjacent carbon. The signals from the two methylene groups (at 6.84 and 7.46) form what is approximately an $A_2X_2$ spectrum. Of the two multiplets, the higher-field one shows evidence of additional splitting and therefore probably represents the methylene group adjacent to the carbon bearing the two $NF_2$ groups. The spectrum is consistent with the following structure: $(NO_2)_3CH_2CH_2C(NF_2)_2CH_3$.

c. Reaction of t-Butyldifluoramine with Sulfuric Acid

A glass bulb (total volume 360 ml) fitted with a monometer and a septum was loaded with 20 ml of concentrated sulfuric acid and was evacuated.

t-Butyldifluoramine (1.0 g, 0.0092 mole) was injected, resulting in an immediate pressure increase to 132 mm. The pressure decreased rapidly, becoming 43 mm in 4 hours and 26 mm (0.0005 mole as a perfect gas) in 2 days. The sulfuric-acid solution was then poured over 100 ml of ice, and the product was extracted vigorously with 20 ml of methylene chloride. The methylene chloride solution was dried over sodium sulfate and was analyzed by infrared spectroscopy. The product was found to be acetone, and measurement of the intensity of the carbonyl peak indicated 0.009 mole of acetone.

d. β-(Difluoramino)butyric Acid

Difluoramine (about 8 g) was refluxed over 2.86 g (0.03 mol , 90% assay) of crotonic acid, and 17 ml of 20% fuming sulfuric acid was added dropwise. The refluxing of the difluoramine was continued for 4-1/2 hours, and the excess difluoramine was then removed. The homogeneous acid solution was poured over 100 ml of ice, and the product was extracted with three 50-ml portions of methylene chloride, was washed with 50 ml of water, and was dried over sodium sulfate. Distillation yielded 1.27 g (0.0091 mole, 34% yield) of β-(difluoramino)butyric acid (bp 58°C/0.8 mm).

Anal. Calcd. for $C_4H_7NF_2O_2$: C, 34.5; H, 5.04; N, 10.1; F, 27.4. Found: C, 34.0; H, 4.64; N, 10.3; F, 27.0.

e. Difluoraminooctane

1-Octene (3.36 g, 0.03 mole) was added over a 45-min period to a refluxing mixture of 15 ml of sulfuric acid and approximately 7 g of difluoramine. When the addition was completed and no further exothermic reaction was evident, the mixture was poured over 300 ml of ice. The product was extracted with five 50-ml portions of methylene chloride. The methylene chloride solution was washed with 100 ml of water and was dried over sodium sulfate, and the solvent was distilled off. Distillation of the residue yielded 0.50 g (9% yield) of crude (90% by gas-chromatographic analysis) difluoraminooctane (bp 40°/4.5 mm). A viscous, undistillable residue (1.9 g) remained. The distillate was purified by gas chromatography to obtain samples for analysis and infrared spectra.

Anal. Calcd. for $C_8H_{17}NF_2$: C, 58.2; H, 10.3; N, 8.50; F, 23.1. Found: C, 57.8; H, 10.4; N, 8.23; F, 23.7.

## B. REACTIONS OF ETHYL N-FLUOROCARBAMATE (V. Grakauskas)

### 1. Discussion

#### a. Acid Hydrolysis

N-Fluorocarbamates are potential starting materials for the preparation of the hitherto unknown fluoramine. Thus, ethyl N-fluorocarbamate might undergo an acid-catalyzed hydrolysis as follows:

$$NHFCOOC_2H_5 \xrightarrow[\Delta]{H_3O^{\oplus}} H_2NF + CO_2 + C_2H_5OH$$

Ethyl N-fluorocarbamate was found to be soluble in concentrated sulfuric acid without decomposition at 25°C. The solutions were stable at 40 to 50°C for several hours. However, a reaction occurred when the ethyl N-fluorocarbamate solution in concentrated sulfuric acid was heated to 60 to 75°C, with the evolution of carbon dioxide. The resulting sulfuric-acid solution underwent no further visible changes even when heated to 95 to 100°C and kept at this temperature for several hours. On attempted distillation at reduced pressures, or extraction with methylene chloride, this sulfuric-acid solution gave only a small amount of diethylsulfate. When this acid solution was poured on ice, the resulting aqueous solution had strong oxidizing properties; however, the oxidizing power gradually faded on standing. At the same time a nonoxidizing gaseous decomposition product was evolved; it failed to absorb in the infrared and was assumed to be nitrogen.

On the basis of the above observations, it was postulated that ethyl N-fluorocarbamate reacted with concentrated sulfuric acid at elevated temperatures, with the formation of either N-fluorosulfamic acid or N-fluoroammonium sulfate:

$$NHFCOOC_2H_5 + H_2SO_4 \longrightarrow NHFSO_3H \quad \text{or} \quad NH_3F^{+}HSO_4^{-}$$

The reaction product with sulfuric acid apparently underwent a rapid hydrolysis to fluoramine when its sulfuric-acid solution was poured on ice:

$$NHFSO_3H + H_2O \longrightarrow [H_2NF] + H_2SO_4$$

or

$$NH_3F^{\oplus} + H_2O \longrightarrow [H_2NF] + H_3O^+$$

The fluoramine apparently was not stable under these conditions and probably decomposed into nitrogen and hydrogen fluoride:

$$2\ H_2NF \longrightarrow N_2 + 2\ HF + 2\ H^+ \text{ (or } H_2)$$

If the above considerations are correct, fluoramine was produced <u>in situ</u> when the sulfuric acid hydrolysis product of ethyl N-fluorocarbamate was diluted with water. To obtain additional evidence in support of these possibilities, an experiment was carried out with the objective of isolating the fluoramine as a derivative. Thus, the sulfuric acid reaction product of ethyl N-fluorocarbamate was poured on a butyraldehyde-ice mixture. It was expected that under these conditions the fluoramine produced <u>in situ</u> would react with the aldehyde, resulting in the formation of either monoadduct or diadduct:

$$C_3H_7CHO + H_2NF \longrightarrow C_3H_7CH(OH)NHF \text{ and/or } C_3H_7CH(NHF)_2$$

These adducts were expected to be more stable than fluoramine itself, and thus capable of isolation. The product of this reaction, however, was identified as <u>n</u>-butyronitrile. Apparently, the expected monoadduct was produced, but it was unstable under these reaction conditions and underwent decomposition to butyronitrile:

$$C_3H_7CHO + H_2NF \xrightarrow{H_3O^+} C_3H_7CH(OH)NHF \xrightarrow{-H_2O} C_3H_7CH{=}NF \xrightarrow{-HF} C_3H_7C{\equiv}N$$

Similar reactions of aromatic aldehydes with chloramine have been reported by Hauser and Gillaspie.*

The reaction of butyraldehyde and fluoramine has been carried under arbitrarily chosen conditions, and it is possible that shorter

*R. C. Hauser and A. G. Gillaspie, <u>J. Am. Chem. Soc.</u>, <u>52</u>, 4517 (1930).

reaction times and lower temperatures will allow the isolation of the intermediates leading to the butyronitrile. The possibility of synthesizing fluorimino compounds from ketones is under investigation. This reaction would not only indicate the presence of fluoramine, but would also provide a new route to fluorimino compounds:

$$RR'C = O + [H_2NF] \xrightarrow{H_3O^{\oplus}} RR'C(OH)NHF \xrightarrow[-H_2O]{} RR'C = NF$$

b. Reactions with Carbonyl Compounds

Reactions of carbamates with carbonyl compounds are described in the literature. Kraft and Herbst* showed that carbamates react with aldehydes to give the corresponding diadducts:

$$RCHO + NH_2COOR' \xrightarrow{H_3O^{+}} RCH(NHCOOR')_2 + H_2O$$

These reactions are catalyzed by catalytic amounts of mineral acids, and only diadducts are obtained. The only monoadduct reported is that of formaldehyde, which is synthesized under basic reaction conditions. The formaldehyde-carbamate monoadducts are not stable in the presence of acids and undergo disproportionation to diadducts. With the exception of pyruvic acid, which gives the corresponding diadduct, ketones do not react with carbamates under these conditions.

Reactions of difluoramine with aldehydes or ketones to give either monoadducts or diadducts, depending on the reaction conditions, are well known.

Monofluorocarbamates can be considered to be structurally similar to carbamates and to difluoramine; they were therefore expected to react with carbonyl compounds.

It was found that ethyl N-fluorocarbamate reacts readily with aqueous formaldehyde to give the corresponding monoadduct quantitatively:

*W. M. Kraft and R. M. Herbst, J. Org. Chem., 10, 483 (1945).

$$NHFCOOC_2H_5 + HCHO \xrightarrow{(H_2O)} HOCH_2\text{-}NFCOOC_2H_5$$

The structure of this material was established on the basis of its elemental analysis, infrared spectrum (Figure 7), proton-NMR spectrum (Figure 8), and $F^{19}$-NMR spectrum (Figure 9). The reaction was carried out at room temperature in the presence of a catalytic amount of hydrochloric acid. Attempts to synthesize the diadduct of formaldehyde by using an excess of N-fluorocarbamate were unsuccessful, and a mixture of monoadduct and unreacted N-fluorocarbamate was isolated. Thus, the reaction of ethyl N-fluorocarbamate with formaldehyde is not analogous to the reaction of ethyl carbamate, but more closely resembles the formaldehyde-difluoramine condensation.

The diadduct of formaldehyde and ethyl N-fluorocarbamate was prepared by a stepwise synthesis. An equimolar mixture of ethyl N-fluorocarbamate and ethyl N-fluoro-N-hydroxymethylcarbamate (monoadduct of formaldehyde) was heated for several hours in the presence of a drop of concentrated hydrochloric acid; this procedure resulted in the preparation of the desired diadduct:

$$NHFCOOC_2H_5 + HOCH_2NFCOOC_2H_5 \xrightarrow[65\text{-}70^\circ C]{H_3O^+} CH_2(NFCOOC_2H_5)_2 + H_2O$$

A quantitative yield of the product in 20% conversion was obtained under these conditions. The product was found to be identical with the high-boiling material, formed in the direct fluorination of diethyl methylenedicarbamate, for which the structure of diethyl N,N'-difluoromethylenedicarbamate had been established.*

Butyraldehyde reacted with ethyl N-fluorocarbamate in the absence of a solvent to give, depending on the reaction conditions, either the monoadduct or the diadduct:

$$\underline{n}\text{-}C_3H_7CHO + HNFCOOC_2H_5 \xrightarrow{H_3O^+} \underline{n}\text{-}C_3H_7CH(OH)NFCOOC_2H_5 \quad \text{or} \quad \underline{n}\text{-}C_3H_7CH(NFCOOC_2H_5)_2$$

*Aerojet-General Report 0235-01-12, December 1961 (Confidential).

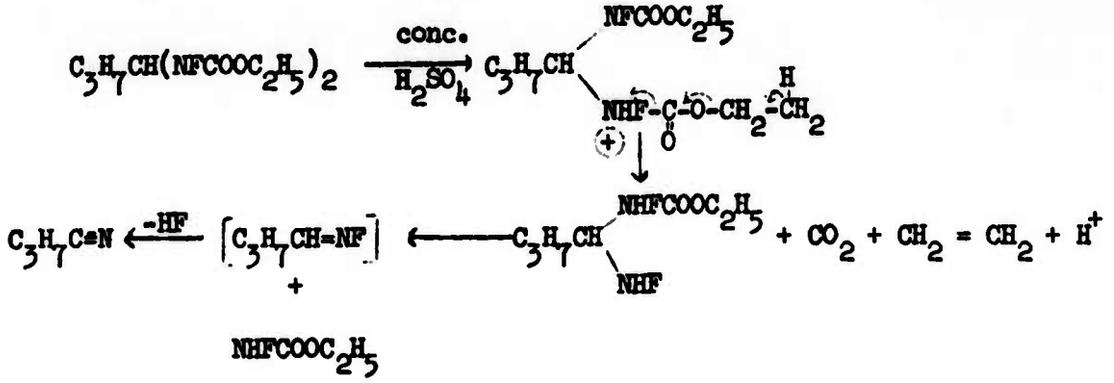
The reaction was catalyzed by a trace of hydrochloric acid. The monoadduct was found to be very unstable, in this case, but its structure was proved by means of the infrared and proton-NMR spectra (Figures 10 and 11, respectively) and elemental analysis. On distillation, or on prolonged standing, the product gradually dissociated to give the starting materials and possibly some diadduct. The diadduct of butyraldehyde was obtained in 80 to 85% yields under reaction conditions that were similar to those used for the preparation of the monoadduct, except that a twofold molar amount of N-fluorocarbamate was used. The structure of the compound was established by means of elemental analysis and infrared and proton-NMR spectra (Figures 12 and 13, respectively). The diadduct was found to be stable on distillation and could be stored for prolonged periods at room temperature without noticeable changes.

Several initial attempts have been made to react ethyl N-fluorocarbamate with ketones to synthesize the corresponding monoadduct or diadduct:

$$RR'CO + NHFCOOC_2H_5 \longrightarrow RR'C(OH)NFCOOC_2H_5 \text{ and/or } RR'C(NFCOOC_2H_5)_2$$

It was found that 3-pentanone does not react with ethyl N-fluorocarbamate under the reaction conditions used to synthesize the monoadducts and diadducts of aldehydes. On the other hand, when the reaction was carried out under the conditions used for the preparation of gem-difluoramino compounds (i.e., in concentrated sulfuric acid, using a 1-to-2 molar ratio of reagents), a vigorous gas evolution resulted even at 0 to 5°C and half of the N-fluorocarbamate was recovered. The gaseous reaction product was found to be a mixture of carbon dioxide and ethylene. The fate of the 3-pentanone in this reaction is not yet known.

A similar reaction occurred when the diadduct of n-butyraldehyde was reacted with concentrated sulfuric acid at 0 to 5°C. In this case, too, a vigorous gas evolution took place and the gaseous reaction product was shown to be a mixture of carbon dioxide and ethylene. n-Butyronitrile and ethyl N-fluorocarbamate, each approximating 1 mole per mole of the starting material, were isolated from the sulfuric-acid solution. The following is a possible mechanism for this reaction:

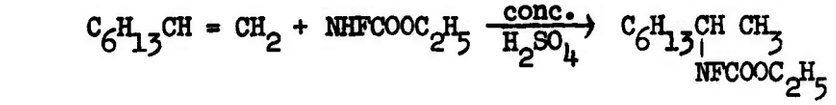


It is possible that the 3-pentanone reaction proceeded by a similar mechanism. On the other hand, it may be that only the monoadduct of the ketone was involved in this reaction and the second mole of ethyl N-fluorocarbamate never entered the reaction sequence.

The reactions of ethyl N-fluorocarbamate with aldehydes showed that N-fluorocarbamates resemble both difluoramine and carbamates in their reactions. In the reaction with formaldehyde, the behavior of ethyl N-fluorocarbamate was similar to that of difluoramine. The reaction of ethyl N-fluorocarbamate with butyraldehyde leading to the diadduct, on the other hand, was more like the reaction of carbamates in that the preparation was achieved under relatively mild reaction conditions with only a catalytic amount of aqueous mineral acid. The formation of the butyraldehyde-N-fluorocarbamate monoadduct was more like the analogous reaction of difluoramine.

c. Reactions with Olefins and Acetylenic Compounds

To further extend the scope of N-fluorocarbamate reactions, the addition of ethyl N-fluorocarbamate to olefinic and acetylenic compounds was investigated. It was found that a concentrated sulfuric acid solution of ethyl N-fluorocarbamate reacted with octene-1 at 5 to 25°C to give a 1-to-1 adduct. The product was identified as ethyl N-fluoro-N-(2-octyl)carbamate:



The infrared spectrum (Figure 14) is consistent with the structure, and the direction of addition was confirmed by the proton-NMR spectrum (Figure 15).

The addition of ethyl N-fluorocarbamate to other types of olefinic compounds was also investigated. Methylacrylate reacted with the sulfuric-acid solution of ethyl N-fluorocarbamate to give a 1-to-1 adduct in 70% yield. The structure of the product was established on the basis of its infrared spectrum (Figure 16) and elemental analysis. The proton-NMR spectrum (Figure 17) showed that the fluorocarbamate moiety added to the methylene carbon atom of the acrylate:

$$CH_2{=}CHCOOCH_3 + NHFCOOC_2H_5 \xrightarrow[H_2SO_4]{\text{conc.}} \underset{\displaystyle NFCOOC_2H_5}{\underset{|}{CH_2CH_2COOCH_3}}$$

A similar mode of addition has been reported for the difluoramine-acrylate reaction.* The structure of the adduct was further proved by conversion to the known methyl β-difluoraminopropionate on direct fluorination:

$$\underset{\displaystyle NFCOOC_2H_5}{\underset{|}{CH_2CH_2COOCH_3}} + F_2 \xrightarrow{(H_2O)} NF_2CH_2CH_2COOCH_3 + CO_2 + C_2H_5OH$$

The reaction of ethyl N-fluorocarbamate with ethyl vinyl ether resulted in high yields of a 1-to-1 adduct. In this case the reaction was carried out in the absence of a solvent and the condensation was catalyzed by a trace of concentrated hydrochloric acid. The composition of the product was established by means of its infrared spectrum (Figure 18) and elemental analyses. The proton-NMR spectrum of the product (Figure 19) indicated the direction of addition, showing that the fluorocarbamate moiety added α to the ether linkage:

$$CH_2 = CHOC_2H_5 + NHFCOOC_2H_5 \xrightarrow{H_3O^+} \underset{\displaystyle NFCOOC_2H_5}{\underset{|}{CH_3CHOC_2H_5}}$$

*Aerojet-General Report 0235-01-11, 14 July 1961 (Confidential).

The $F^{19}$-NMR spectrum is shown in Figure 20.

Only preliminary results are available on the reaction between ethyl N-fluorocarbamate and acetylenic compounds. The reaction was carried out in concentrated sulfuric acid with hexyne-3 as a model compound. A highly exothermic reaction, accompanied by a vigorous gas evolution, occurred when hexyne-3 was added to an ethyl N-fluorocarbamate solution in concentrated sulfuric acid at 0 to 5°C. In general, this reaction appeared similar to that of 3-pentanone. The gaseous reaction product was identified as a mixture of carbon dioxide and ethylene, and roughly half of the carbamate was recovered from the sulfuric-acid solution at the end of the run. The fate of hexyne-3 in the reaction has not yet been determined.

The further extension of the reactions of N-fluorocarbamate with unsaturated compounds is under investigation.

2. Experimental

a. Ethyl N-Fluorocarbamate

Ethyl N-fluorocarbamate was prepared by the fluorination of aqueous ethyl carbamate as previously described.* Several 3-mole batches of ethyl carbamate were fluorinated, and the product was purified by fractional distillation or by conversion to its sodium salt.** The refractive index previously reported should be corrected to $n_D^{25}$ 1.3972.

b. Reaction of Ethyl N-Fluorocarbamate with Sulfuric Acid

Concentrated sulfuric acid (15 ml) was placed in a 25-ml, three-necked, round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a small dropping funnel containing 5.0 g of ethyl N-fluorocarbamate. The carbamate was added to sulfuric acid, with stirring, at 15 to 20°C over a period of 5 min. The material dissolved readily in sulfuric acid, with only

*High-Energy Oxidizer Binders for Solid Propellants, Aerojet-General Report 0371-02-3, 14 October 1960 (Confidential).

**Aerojet-General Report 0235-01-11, July 1961 (Confidential).

slight evolution of heat. The dropping funnel was removed and the reactor was connected in series with a -80°C trap and an evacuated infrared gas cell. The sulfuric-acid solution was heated gradually until vigorous gas evolution began at 60 to 75°C. The solution was kept at 65 to 70°C until gas evolution ceased after 15 to 20 min. The gaseous reaction products passed through a -80°C trap without condensing. The infrared spectrum of this gas indicated a mixture of carbon dioxide and ethylene. The sulfuric acid was then heated to 90 to 100°C and was kept at this temperature for an additional 15 min.

The reaction mixture was vacuum-distilled at a pot temperature of 90 to 100°C/0.1 to 0.3 mm. A small amount (0.1 to 0.2 g) of colorless liquid distilled over and was identified as diethylsulfate by its infrared spectrum.

At the end of the distillation, the reaction mixture was cooled to room temperature and was extracted with five 15-ml portions of methylene chloride. The combined extracts were concentrated, and the residue was distilled to give an additional 0.2 to 0.3 g of diethylsulfate.

The residual methylene chloride was removed from the reaction mixture at reduced pressure, and the sulfuric-acid solution was poured onto 100 g of ice. The resulting, colorless, aqueous solution had strong oxidizing properties when tested with potassium iodide-starch paper. On standing for 5 to 10 min the solution began to evolve nonoxidizing gaseous products. The rate of gas evolution increased when the mixture was allowed to warm to room temperature. At this point the reaction mixture was placed in a 150-ml round-bottomed flask, and the flask was connected in series with a -80°C trap and an evacuated infrared gas cell. The gaseous reaction products passed through the -80°C trap, and the 10-cm infrared gas cell was filled to a pressure of 500 mm Hg. The material failed to absorb in the infrared and was therefore assumed to be nitrogen.

The gradual gas evolution continued for 2 to 3 hours. At the end of this period the reaction mixture was allowed to stand at room temperature overnight. The mixture did not then evolve gas, nor did it oxidize potassium iodide.

c. Reaction with Butyraldehyde

A solution of 4.3 g of ethyl N-fluorocarbamate (0.04 mole) in 25 ml of concentrated sulfuric acid was heated at 65 to 95°C, as described above. The resulting solution was cooled to 10 to 15°C and was poured on a mixture of 1.44 g of butyraldehyde (0.02 mole) and 80 g of crushed ice. The mixture was allowed to warm gradually to room temperature and to stand at 25 to 27°C for 18 hours. At the end of this time, the mixture (nonoxidizing) was extracted with four 20-ml portions of methylene chloride. The combined extracts were dried, and the filtered solution was concentrated to remove the solvent. The residue was distilled at reduced pressure to give 1.1 g of a colorless liquid that was identified as n-butyronitrile by means of its infrared spectrum.

d. Ethyl N-Fluoro-N-hydroxymethylcarbamate

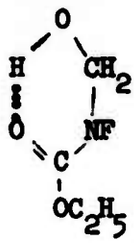
(1) Excess of Formaldehyde

Five drops of concentrated hydrochloric acid and 6.42 g of ethyl N-fluorocarbamate (0.06 mole) were added to a solution of 25 ml of 37% aqueous formaldehyde in 50 ml of water, at 5 to 10°C. The reaction mixture was allowed to rise gradually to room temperature after 16 hours. The mixture was extracted with six 30-ml portions of methylene chloride, the combined extracts were dried with Drierite and were filtered, and the filtrate was concentrated. The residue, a pale-yellow liquid, was purified by distillation to give 6.8 g of a colorless liquid (bp 40 to 44°C/0.1 to 0.3 mm, $n_D^{25}$ 1.4160). The material was redistilled and a middle cut (bp 43°C/0.1 to 0.3 mm, $n_D^{25}$ 1.4180) was taken for analysis.

Anal. Calcd. for $HOCH_2NFCOOC_2H_5$, $C_4H_8FNO_3$: C, 35.04; H, 5.9; F, 13.9; N, 10.2. Found: C, 35.0; H, 5.98; F, 13.8; N, 10.35.

The infrared spectrum (Figure 7) was obtained for the material as a thin film and as a solution in carbon tetrachloride. The thin film shows a strong bond at 5.77 microns with a shoulder at 5.70 micron (assigned to C=O). A broad band appears at 2.92 microns (assigned to H-bonded OH). In the carbon tetrachloride solution the C=O bond is split (5.80 and 5.65 microns)

and a sharp bond appears at 2.8 microns (assigned to free OH). This behavior suggests the presence of a hydrogen-bonded cyclic structure:



The proton-NMR spectrum (Figure 8) was obtained in carbon tetrachloride solution, with TMS as an internal reference. The O<u>H</u> signal appears at 4.97 ($\tau$ value) bracketed by a doublet (4.64 and 5.19) that is assigned to the HOC<u>H</u>$_2$NF-protons (split 33 cps by the adjacent NF). There is apparently no coupling between the <u>H</u>OCH$_2$- and HOC<u>H</u>$_2$- protons. The ester ethyl triplet and quartet appear at 8.63 and 5.67, respectively.

The $F^{19}$-NMR spectrum (Figure 9) was obtained in carbon tetrachloride solution, with Freon-11 added as an internal reference. The spectrum consists of a single signal: a triplet at +74.9 ppm from Freon-11. It is assigned to HOCH$_2$N<u>F</u>COOEt (split by the adjacent methylene group).

(2) Excess of Ethyl N-Fluorocarbamate

To a solution of 2.43 g of 37% aqueous formaldehyde (0.89 g or 0.03 mole of HCHO) in 25 ml of water was added at 25°C, with stirring, 6.45 g of ethyl N-fluorocarbamate (0.06 mole). No visible reaction was noted. After a few minutes, 1.0 ml of 50% sulfuric acid was added and the mixture was allowed to stand at 25 to 28°C for 20 hours. At the end of this period the solution was extracted with six 25-ml portions of methylene chloride. The dried and filtered methylene chloride solution was concentrated; after removal of the solvent, the residual liquid was fractionated to give two products: one of bp 28 to 31°C/0.1 to 0.3 mm and $n_D^{25}$ 1.3975 (3.1 g), and the other of bp 42 to 43°C/ 0.1 to 0.3 mm and $n_D^{25}$ 1.4178 (3.2 g). Infrared spectra indicated that the material of the first fraction was the unreacted ethyl N-fluorocarbamate, and that of the second fraction was ethyl N-fluoro-N-hydroxymethylcarbamate.

e. Diethyl N,N'-Difluoromethylenedicarbamate

Two drops of concentrated hydrochloric acid were added, at 20 to 25°C, to a mixture of 6.85 g of ethyl N-fluoro-N-hydroxymethylcarbamate (0.05 mole) and 5.4 g of ethyl N-fluorocarbamate. No visible reaction occurred. The mixture was then warmed to 60 to 65°C and allowed to stand at that temperature for 16 hours. At the end of this period, the mixture was fractionated; after the removal of small amounts of water mixed with an unidentified volatile liquid, the residual liquid was fractionated to give 4.5 g of ethyl N-fluorocarbamate ($n_D^{25}$ 1.3975), 3.4 g of ethyl N-fluoro-N-hydroxymethylcarbamate ($n_D^{25}$ 1.4180), and 2.3 g of a colorless liquid (bp 83 to 84°C/0.1 to 0.3 mm, $n_D^{25}$ 1.4240). This high-boiling product was identified as diethyl N,N'-difluoromethylenedicarbamate by means of its infrared spectrum and physical properties.* The yield was 20%, on the basis of consumed ethyl N-fluorocarbamate.

f. Reactions of Butyraldehyde and Ethyl N-Fluorocarbamate

(1) Preparation of $\underline{n}$-$C_3H_7CH(OH)NFCOOC_2H_5$

To a mixture of 5.5 g of butyraldehyde (0.076 mole) and 4.3 g of ethyl N-fluorocarbamate (0.04 mole) was added one drop of concentrated hydrochloric acid. Cooling was necessary to keep the reaction temperature at 25 to 30°C. When the initial exothermic reaction subsided, the cooling bath was removed and the reaction mixture was allowed to stand at 25 to 27°C for 16 hours. At the end of this period, the reaction mixture was subjected to fractional distillation. After removal of the unreacted butyraldehyde and traces of moisture, the bulk of the material boiled at 63 to 67°C/0.1 to 0.3 mm to give 5.5 g of a colorless liquid ($n_D^{25}$ 1.4120). A distillation residue of 1.8 g was not further investigated.

A sample of the material with $n_D^{25}$ 1.4120 was submitted for infrared, NMR, and elemental analysis.

Anal. Calcd. for $C_3H_7CH(OH)NFCOOC_2H_5$, $C_7H_{14}FNO_3$: C, 46.92; H, 7.88; F, 10.60; N, 7.82. Found: C, 47.50; H, 8.46; F, 10.80; N, 7.53.

*Aerojet-General Report 0235-01-12, December 1961, p. 14 (Confidential).

The infrared spectrum (Figure 10) showed that the material was probably contaminated with starting materials (see the complex absorption in the NH-OH stretching region). The proton-NMR spectrum was obtained in carbon tetrachloride solution (Figure 11), with TMS as an internal reference. The ester ethyl triplet and quartet are seen at 5.67 and 8.65 ($\tau$ value), respectively. Butyraldehyde is present as evidenced by the signal at 0.04 (-CHO) and the broad multiplet under the ester ethyl triplet at 8.65. The pair of triplets centered on 4.69 may be assigned to the $-CH_2\underline{C}H-NF$ proton of the proposed structure. The signal at 5.47 seems to be the hydroxylic proton.

(2) Preparation of $\underline{n}\text{-}C_3H_7CH(NFCOOC_2H_5)_2$

Two drops of concentrated hydrochloric acid were added, at 25 to 30°C, to a mixture of 10.7 g of ethyl N-fluorocarbamate (0.1 mole) and 3.6 g of butyraldehyde (0.05 mole). Cooling was required to keep the temperature below 45 to 50°C; the heat evolution ceased 5 min after mixing. The reaction mixture was warmed to 55 to 65°C and was allowed to stand at that temperature for 18 hours; it was then subjected to fractional distillation. After the removal of 1.2 g of volatile materials (mainly water and unreacted butyraldehyde), 3.2 g of unreacted ethyl N-fluorocarbamate ($n_D^{25}$ 1.3980) was recovered. Further distillation gave 8.1 g of a colorless liquid (bp 81 to 82°C/ 0.1 to 0.2 mm, $n_D^{25}$ 1.4272). The distillation residue amounted to 0.7 g and was discarded.

Anal. Calcd. for $C_3H_7CH(NFCOOC_2H_5)_2$, $C_{10}H_{18}F_2N_2O_4$: C, 44.77; H, 6.77; F, 14.16; N, 10.44. Found: C, 45.10; H, 6.53; F, 14.4; N, 10.32.

The yield of the product was 86%, and the conversion was 60%. The infrared spectrum (Figure 12) is consistent with the structure. The proton-NMR spectrum (Figure 13) was obtained in carbon tetrachloride solution, with TMS as an internal reference. The triplet and quartet of the ester ethyl groups are found at 8.66 and 5.67 ($\tau$ value), respectively. The triplet is superimposed on a broader, more-complicated signal attributable to the $C_3H_7CH$ group. A triplet of triplets to the low-field side of the ethyl methylene quartet (centered at 4.06) may be assigned to the $C_2H_5CH_2\underline{C}H$ proton (split about 35 cps by two adjacent fluorines and about 8.7 cps by the adjacent $CH_2$.

g. Reaction of Ethyl N-Fluorocarbamate and 3-Pentanone

To a solution of 5.4 g of ethyl N-fluorocarbamate (0.05 mole) in 25 ml of concentrated sulfuric acid was added dropwise, at 0 to 5°C and with stirring, 2.15 g of 3-pentanone (0.025 mole) over a period of 25 min. The reaction was exothermic, and the reaction flask was cooled externally. The gaseous product evolved during the reaction passed without condensing through a -80°C trap; a sample of it was trapped in an evacuated infrared gas cell, and the product was shown to be a mixture of carbon dioxide and ethylene.

At the end of the run the sulfuric-acid solution was poured on 70 g of crushed ice, and the resulting aqueous solution was extracted with six 50-ml portions of methylene chloride. The methylene chloride extracts were combined, were dried with Drierite, and were filtered, and the filtrate was concentrated to remove the solvent. The residual liquid was distilled to give 2.2 g of a colorless liquid (bp 28 to 31°C/0.1 to 0.3 mm, $n_D^{25}$ 1.3970). This material was identified by means of its infrared spectrum as ethyl N-fluorocarbamate.

h. Reaction of $\underline{n}$-$C_3H_7CH(NFCOOC_2H_5)_2$ with Concentrated Sulfuric Acid

Concentrated sulfuric acid (15 ml) was placed in a 25-ml, three-necked, round-bottomed, reaction flask equipped with a thermometer, a mechanical stirrer, and a small dropping funnel containing 4.0 g of $\underline{n}$-$CH_3H_7CH(NFCOOC_2H_5)_2$ (0.015 mole). The reactor was connected in series with an -80°C trap and an evacuated infrared gas cell through the top of the dropping funnel. The sulfuric acid was cooled to 5 to 10°C; to it was added, with stirring, $C_3H_7CH(NFCOOEt)_2$ from the dropping funnel over a period of 25 min. The reaction mixture evolved a gaseous product that failed to liquefy in the -80°C trap; a sample of it was trapped in the infrared gas cell and was found to be a mixture of carbon dioxide and ethylene.

At the end of the reaction, the orange-red sulfuric-acid solution was poured onto 50 g of crushed ice and the resulting aqueous solution was extracted with four 20-ml portions of methylene chloride. The combined

extracts were dried with Drierite, were filtered, and were concentrated to remove the solvent. The residual, dark liquid was fractionated to give 0.4 g of a colorless liquid (bp 28 to 30°C/20 to 25 mm) and 0.9 g of another colorless liquid (bp 28 to 30°C/0.1 to 0.3 mm, $n_D^{25}$ 1.3970). By means of its infrared spectrum, the former product was identified as butyronitrile; similarly, the latter product was found to be ethyl N-fluorocarbamate. A viscous, dark, distillation residue (bp >95°C/0.1 mm) amounted to 0.8 g.

i. Preparation of $C_6H_{13}CH(CH_3)NFCOOC_2H_5$

To a solution of 5.4 g of ethyl N-fluorocarbamate (0.05 mole) in 25 ml of concentrated sulfuric acid was added 5.6 g of octene-1 (0.05 mole) at 5 to 10°C with stirring over a period of 15 min. The reaction was exothermic, and the reaction flask was cooled externally by means of an ice-water bath. At the end of the addition, the reaction mixture was kept at 5 to 10°C for an additional 10 min, and was then allowed to warm to 25 to 27°C. After standing for 10 min at that temperature, the mixture was cooled to 5 to 10°C and was poured on 80 g of crushed ice. The water-insoluble oil was extracted with three 25-ml portions of methylene chloride. The combined methylene chloride extracts were dried over Drierite and were filtered, and the filtrate was concentrated. The residual, somewhat-dark liquid was purified by distillation. After the removal of a small forerun (0.8 g, $n_D^{25}$ 1.4195), the bulk of the material boiled at 58 to 59°C/0.1 mm to give 8.1 g of a colorless liquid ($n_D^{25}$ 1.4262). A small distillation residue (0.6 g, $n_D^{25}$ 1.4322) was discarded.

Anal. Calcd. for $C_6H_{13}CH(CH_3)NFCOOC_2H_5$, $C_{11}H_{22}FNO_2$: C, 60.24; H, 10.11; F, 8.66; N, 6.39. Found: C, 60.60; H, 10.5; F, 9.3; N, 6.52.

The proton-NMR spectrum was obtained in carbon tetrachloride solution (Figure 15), with TMS as an internal reference. The spectrum was also compared with that of ethyl N-fluoro-N-methylcarbamate (Figure 21). The spectrum of $CH_3NFCOOC_2H_5$ showed a triplet and a quartet of the ethyl group at 8.69 and 5.86 ($\tau$ values), respectively. The $CH_3NF$ group is a doublet (split approximately 28 cps by the adjacent NF) centered at 6.71. The $F^{19}$-NMR spectrum of ethyl N-fluoro-N-methylcarbamate (Figure 22) was also obtained. In

$C_6H_{13}CH(CH_3)NFCOOC_2H_5$ the triplet and quartet of the ethyl group appear at 8.70 and 5.77, respectively. The triplet is superimposed on a broader, more-complicated signal, which is presumably for the $C_6H_{13}$ group. A weak signal appears to the high-field side of the ethyl methylene quartet. When examined at a higher radio-frequency level and with a slower sweep, it appears to be one of a pair of multiplets, the other of which is buried under the methylene quartet. Thus, the weak signal may be assigned to the CHNF proton (split into two sextets (?) by adjacent protons and NF). The spectrum is consistent with the assigned structure.

j. Methyl N-Carbethoxy-N-fluoro-β-aminopropionate

The reaction of methyl acrylate (4.3 g, 0.05 mole) and a concentrated-sulfuric-acid (20-ml) solution of ethyl N-fluorocarbamate (5.4 g, 0.05 mole) was carried out under essentially the same reaction conditions described for octene-1 addition. At the end of the run the sulfuric-acid solution of the product was poured onto 100 g of crushed ice, and the resulting aqueous mixture was extracted with four 30-ml portions of methylene chloride. The combined methylene chloride extracts were dried with Drierite and were filtered, and the filtrate was concentrated to remove the solvent. The residual liquid was fractionated; after the removal of some unreacted acrylate and 1.3 g of unreacted ethyl N-fluorocarbamate, 5.1 g of a colorless liquid (bp 52 to 54°C/ 0.1 to 0.3 mm, $n_D^{25}$ 1.4235) was obtained (50% yield, 70% conversion).

Anal. Calcd. for $C_7H_{12}FNO_4$: C, 43.52; H, 6.26; F, 9.84; N, 7.25. Found: C, 43.3; H, 6.17; F, 10.2; N, 7.15.

The infrared and proton-NMR spectra (Figures 16 and 17, respectively) are consistent with the structure. The proton-NMR spectrum was obtained in carbon tetrachloride solution, with TMS as an internal reference. The ester ethyl triplet and quartet are found at 8.65 and 5.77 ($\tau$ values), respectively. The relative intensities in the quartet are distorted from the expected 1:3:3:1 ratio. The triplet at 7.35 is assigned to the $CH_2CO_2CH_3$ proton (split by the adjacent $CH_2$). The signal from the $-NFCH_2CH_2CO_2CH_3$

protons is expected to be a pair of triplets (split about 30 cps by the adjacent NF) with the same relative intensities and spacings. One such triplet is seen at 6.35. The increased relative intensity of the central member may be attributed to a coincidence with it of the $-CO_2CH_3$ signal. The other of the pair of triplets is overlapped by the ester ethyl quartet but may be partially resolved from it, as shown by the spectra recorded with a reduced sweep rate. The spectrum is thus consistent with the assigned structure.

The reaction of acrylate and carbamate did not take place at 10 to 15°C, and unreacted starting materials were recovered. The condensation described above was achieved by allowing the sulfuric-acid solution of the components to warm to 25 to 28°C and keeping it at that temperature for 90 min.

k. Ethyl N-Fluoro-N-(α-ethoxy)ethylcarbamate

To a mixture of 5.4 g of ethyl N-fluorocarbamate (0.05 mole) and 3.6 g of ethyl vinyl ether (0.05 mole) at 20°C was added one drop of concentrated hydrochloric acid. The reaction temperature began to increase immediately, and dry-ice acetone cooling was applied to keep the reaction temperature at 35 to 45°C. After 5 to 10 min, the exothermic reaction ceased. The cooling bath was removed and the reaction mixture was allowed to cool from 40°C to 25°C (15 min). The reaction mixture was fractionated; after the removal of a small forerun (0.7 g), 7.5 g of a colorless liquid distilled at 35 to 36°C/0.1 to 0.3 mm ($n_D^{25}$ 1.4194). A small distillation residue was discarded.

On the basis of the elemental analysis it was determined that the $n_D^{25}$ 1.4194 fraction was a mixture containing approximately 5 to 7% of ethyl N-fluorocarbamate and 95 to 93% of its adduct. This finding was confirmed by the results of gas-chromatographic analysis. The contamination of the product with the unreacted ethyl N-fluorocarbamate probably could have been avoided by using a slight excess of ethyl vinyl ether in the reaction. An analytical sample of the adduct was isolated by gas chromatography.

Anal. Calcd. for $C_7H_{14}FNO_3$: C, 46.92; H, 7.88; N, 7.81; F, 10.60. Found: C, 46.4: H, 7.8; N, 7.9; F, 10.8.

The proton-NMR spectrum (Figure 19) was obtained in carbon tetrachloride, with TMS as an internal reference; it is consistent with the structure. The $CH_3\underline{C}\underline{H}\underline{N}F$ signal consists of a pair of quartets of 4.45 and 5.07 ($\tau$ values). This structure would be expected as a result of splitting by the adjacent $\underline{CH}_3$ (producing a quartet) and $\underline{N}\underline{F}$ (splitting the quartet into a pair). The ester methylene quartet is seen at 5.74. The multiplet to the high-field side is assigned to the ether methylene. The anomalous splitting is apparently characteristic of $C_2H_5OCR_3$. The complex multiplet centered at 8.65 consists of the overlapping signals from the methyls of the two ethyl groups. One normal triplet may be found; it is assigned to the ester methyl. The other triplet shows anomalous splitting and is assigned to the ether methyl group. The spectrum is thus consistent with the suggested structure, and the alternative structure ($C_2H_5OCH_2CH_2NFCOOEt$) may be ruled out.

The $F^{19}$-NMR spectrum (Figure 20) was obtained in carbon tetrachloride solution, with Freon-11 added as an internal reference. The spectrum consists of a single signal: a doublet at +96.3 ppm from Freon-11. It is assigned to $C_2H_5OCH(CH_3)\underline{N}\underline{F}COOC_2H_5$ (split by the proton on the tertiary carbon atom).

1. Reaction of Ethyl N-Fluorocarbamate and Hexyne-3

The reaction of hexyne-3 (2.0 g, 0.025 mole) and a sulfuric-acid (25-ml) solution of ethyl N-fluorocarbamate (5.4 g, 0.05 mole) was carried out at 5 to 10°C in essentially the same manner as described for the similar reaction of 3-pentanone.

A vigorous evolution of gaseous reaction products, non-condensable at -80°C, occurred from the beginning of the run. The gaseous product was identified (infrared spectrum) as a mixture of carbon dioxide and ethylene. At the end of the run (15 min), the yellow sulfuric-acid solution was poured onto 100 g of crushed ice and the resulting aqueous solution was extracted with five 30-ml portions of methylene chloride. The combined methylene chloride extracts were dried with Drierite, were filtered, and were concentrated. The distillation of the residual liquid gave 2.5 g of ethyl N-fluorocarbamate

(identified by means of its infrared spectrum). Less than 1 g of a higher-boiling liquid (bp 65 to 68°C/0.3 mm, $n_D^{25}$ 1.4342) was isolated on further distillation, but this material has not yet been identified.

## C. FLUORINATION STUDIES (V. Grakauskas)

### 1. Discussion

The fluorination studies performed during this report period were directed toward the extension of the direct fluorination of aqueous carbamates. This emphasis arose mainly because a variety of N-fluorocarbamates became available from the reactions of ethyl N-fluorocarbamate with aldehydes and olefinic compounds. The objective of these studies was to determine if carbethoxy groups of these derivatives could be replaced selectively by fluorine, with the concomitant formation of the corresponding difluoramino derivatives.

The possibility of the replacement of carbethoxy groups by fluorine has been demonstrated in work on the fluorination of diethyl methylenecarbamate and ethylenedicarbamate.* In these cases, however, it was found that only trace amounts of bis(difluoramino)methane and 1,2-bis(difluoramino)ethane, respectively, were obtained; it was therefore concluded that difluoramino groups deactivate the NHCOOR or NFCOOR groups toward further fluorination. This conclusion was further confirmed by the results of the present work. It was found that the fluorination of aqueous butyraldehyde-N-fluorocarbamate diadduct $[C_3H_7CH(NFCOOC_2H_5)_2]$ did not give the desired 1,1-bis(difluoramino)butane, but the reaction stopped at the monodifluoramino stage, even when excessive amounts of fluorine were used:

$$\underline{n}\text{-}C_3H_7CH(NFCOOC_2H_5)_2 + F_2 \xrightarrow{(H_2O)} \underline{n}\text{-}C_3H_7CH(NF_2)NFCOOC_2H_5$$

The infrared spectrum (Figure 23), proton-NMR spectrum (Figure 24), and $F^{19}$-NMR spectrum (Figure 25) are consistent with the above structure.

The fluorination of aqueous octene-1-N-fluorocarbamate adduct $[C_6H_{13}CH(CH_3)NFCOOC_2H_5]$ resulted in the removal of the carbethoxy group, as evidenced by the infrared spectrum, but the desired 2-difluoraminooctane could

*Aerojet-General Report 0235-01-12, December 1961 (Confidential).

not be isolated. Instead, the compound apparently underwent further fluorination, resulting in the introduction of additional fluoro groups in the molecule, as indicated by the elemental analysis. The product of this reaction has not been characterized; it is probably a mixture of polyfluoro-2-aminooctanes.

2. Experimental

a. Preparation of $\underline{n}$-$C_3H_7CH(NF_2)NFCOOC_2H_5$

A solution (partially a suspension) of 5.4 g of $\underline{n}$-$C_3H_7CH(NFCOOEt)_2$ (0.02 mole) in 350 ml of water was fluorinated at 0 to 5°C with elementary fluorine (diluted with fourfold nitrogen) until approximately 1.5 liters of fluorine gas was consumed. The aqueous mixture was extracted with six 20-ml portions of methylene chloride, the combined extracts were dried with Drierite and were filtered, and the filtrate was distilled to remove the solvent. The residual liquid was fractionated at 40 to 70°C/20 to 25 mm to give 0.7 g of a colorless liquid ($n_D^{25}$ 1.4018), and 1.0 g of a colorless liquid (bp 100 to 110°C/0.1 to 0.3 mm, $n_D^{25}$ 1.4222) was then distilled. The structure of the high-boiling material has not been established. The lower-boiling product ($n_D^{25}$ 1.4018) was found to be $C_3H_7CH(NF_2)NFCOOC_2H_5$.

Anal. Calcd. for $C_7H_{13}F_3N_2O_2$: C, 39.25; H, 6.12; F, 26.61; N, 13.1. Found: C, 40.0; H, 6.1; F, 25.6; N, 12.1.

The infrared spectrum (Figure 23), proton-NMR spectrum (Figure 24), and $F^{19}$-NMR spectrum (Figure 25) are consistent with the above structure. The proton-NMR spectrum was obtained in carbon tetrachloride solution, with TMS as an internal reference. The triplet and quartet of the ester ethyl group appear at 8.60 and 5.60 ($\tau$ values), respectively. The triplet is superimposed on a more complicated multiplet that may be assigned to the $CH_3CH_2CH_2$ group. A broad, weak signal appears to the low-field side of the quartet. When this signal is examined at a higher radio-frequency level and with an increased sweep speed, it is seen to be a complicated but rather symmetrical multiplet. Although the individual absorptions cannot be assigned in detail, the form of the signal is approximately what would be expected for $-CH_2\underline{CH}NF_2(NF-)$. The $\underline{CH}$ signal would be split into a triplet by the adjacent $CH_2$ (expected splitting,

5 to 10 cps). These signals would themselves be split into a triplet by the $NF_2$ group (expected splitting about 30 cps). Thus, the signal becomes very complex. The spectrum therefore supports the proposed structure, but not as clearly as might be desired.

The $F^{19}$-NMR spectrum was obtained in carbon tetrachloride solution, with added Freon-11 as an internal reference. Two signals were observed, the one at -34.0 ppm being about twice the intensity of the one at +89.2 ppm. The signal at -34.0 ppm consists of two close lying doublets. It is assigned to the $-NF_2$ group by virtue of the chemical shift. The interpretation of the splitting is not obvious; the splitting may be the result of coupling to the adjacent CH and the more distant -NFCOOEt. The signal at +89.2 ppm consists of two close-lying triplets. It may be assigned to NFCOOEt by virtue of the chemical shift. The splitting may be the result of coupling to CH and $NF_2$. The chemical shifts and intensity ratios are consistent with the structure. The only questionable point is the necessity to assume appreciable coupling between the rather distant NF and $NF_2$ fluorines.

b. Fluorination of $\begin{matrix} CH_2CH_2COOCH_3 \\ | \\ NFCOOC_2H_5 \end{matrix}$

A solution of 3.2 g of methyl N-carbethoxy-N-fluoro-β-aminopropionate (0.0166 mole) in 200 ml of water was fluorinated at 0 to 5°C with elementary fluorine (diluted fourfold with nitrogen) until approximately 0.5 liter of fluorine gas was consumed. The aqueous solution was extracted with six 15-ml portions of methylene chloride, and the combined extracts were dried, filtered, and concentrated. The residue was fractionated to give 0.7 g of a colorless liquid (bp 47 to 48°C/20 mm, $n_D^{25}$ 1.3794), which was identified as methyl β-difluoraminopropionate by comparing its physical properties and infrared spectrum with those of the known material. The yield was 30%.

c. Fluorination of $C_6H_{13}CH(CH_3)NFCOOC_2H_5$

A solution of 5.7 g of ethyl N-fluoro-N-(2-octyl) carbamate in 350 ml of water was fluorinated, as described in the previous

experiment, until about 3 liters of fluorine gas was passed into the reaction mixture. At the end of the run the aqueous reaction mixture was extracted with four 20-ml portions of methylene chloride, the combined extracts were dried with Drierite and were filtered, and the filtrate was concentrated. The residual liquid was distilled to give 2.2 g of a colorless liquid (bp 25 to 32°C/0.2 to 0.3 mm, $n_D^{25}$ 1.3892). Elemental and gas-chromatographic analyses showed that the product is a mixture containing several compounds.

Anal. Found: F, 36.5; N, 4.95.

## III. CONCLUSIONS

A. By the proper choice of experimental conditions, the alkylation of difluoramine can be extended to both more-reactive and less-reactive substrates than had been indicated by previous work.

B. The acidic hydrogen of N-fluorocarbamate esters may be utilized to prepare adducts of carbonyl and unsaturated compounds. Ester cleavage resulted in the isolation of a derivative of fluoramine.

## IV. FUTURE PLANS

Reactions of difluoramine and fluorocarbamates and the aqueous-fluorination reaction will be studied further.

## V. PERSONNEL

The experimental work was performed by M. A. Sims, M. P. Mascari, G. L. Gable, D. Trowbridge, V. Grakauskas, and K. Baum. Analytical support was provided by K. Inouye, H. Nelson, D. I. Matson, and H. W. Pust.

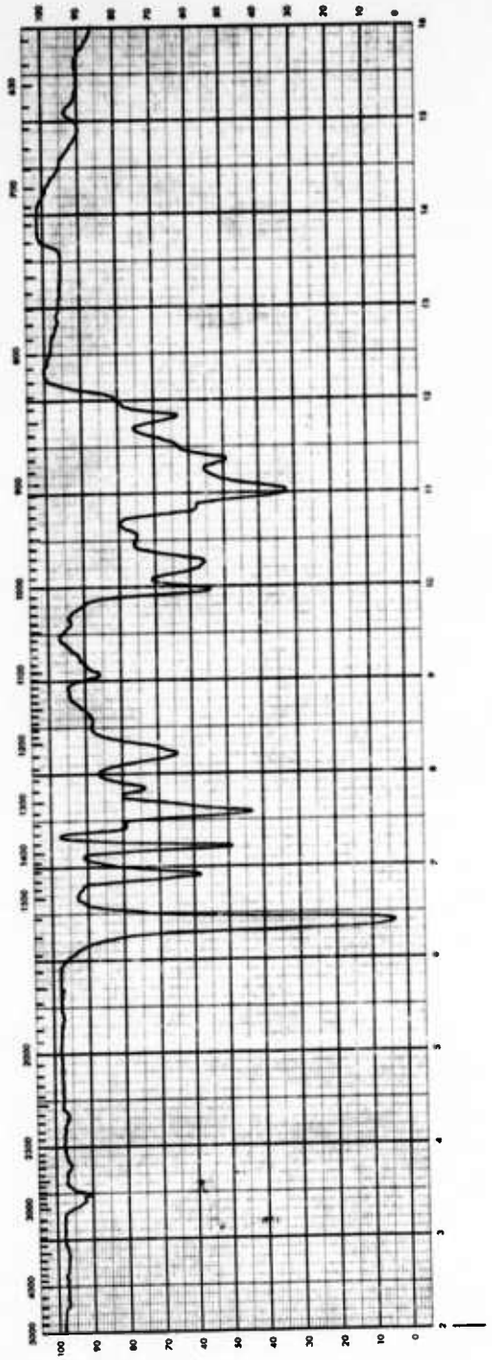


Fig. 1 Infrared Spectrum of 5,5-Dinitro-2,2-bis(difluoramino)hexane

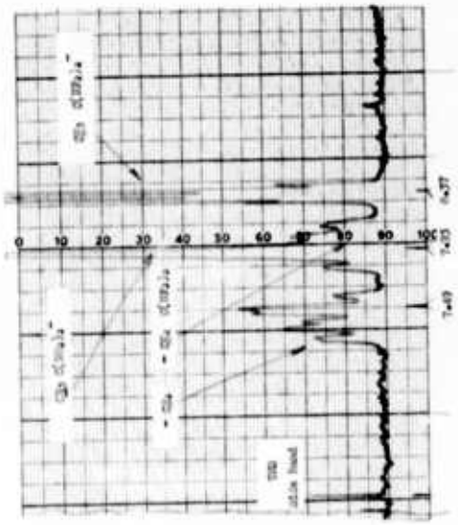


Fig. 2 Proton-NMR spectrum of 5,5-Dinitro-2,2-bis(difluoramino)hexane

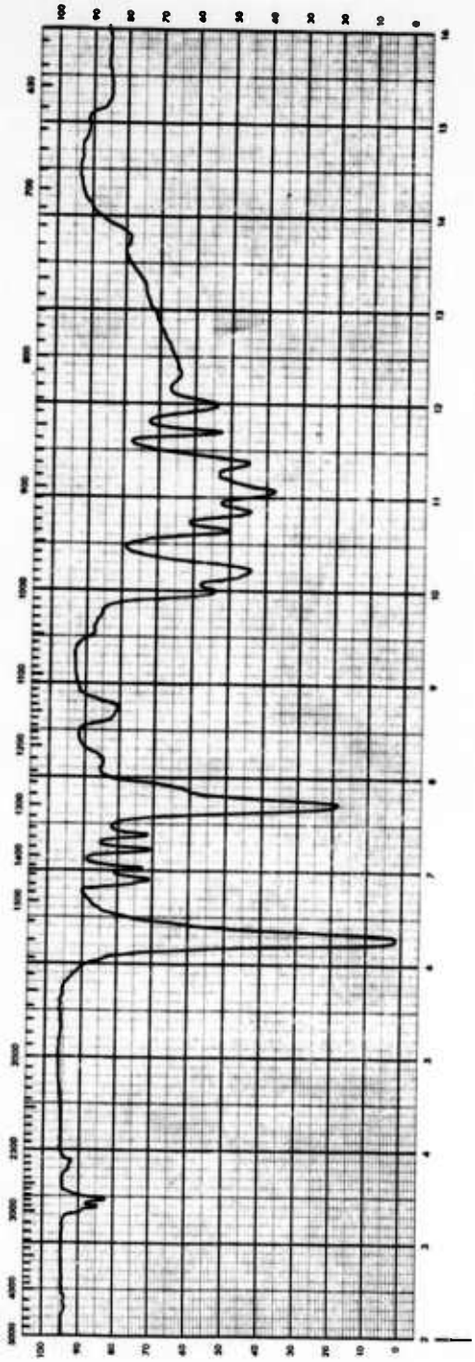


Fig. 3 Infrared Spectrum of 5,5,5-Trinitro-2,2-bis(difluoramino)pentane

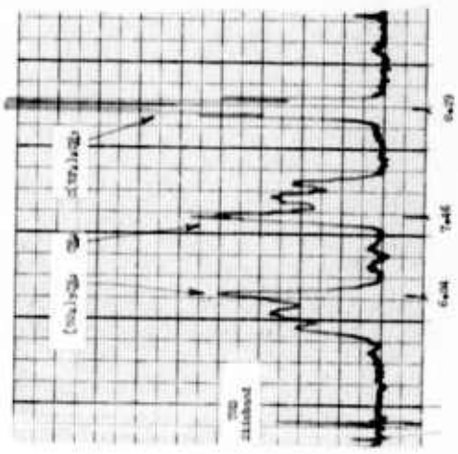


Fig. 4 Proton-NMR Spectrum of 5,5,5-Trinitro-2,2-bis(difluoramino)penatane

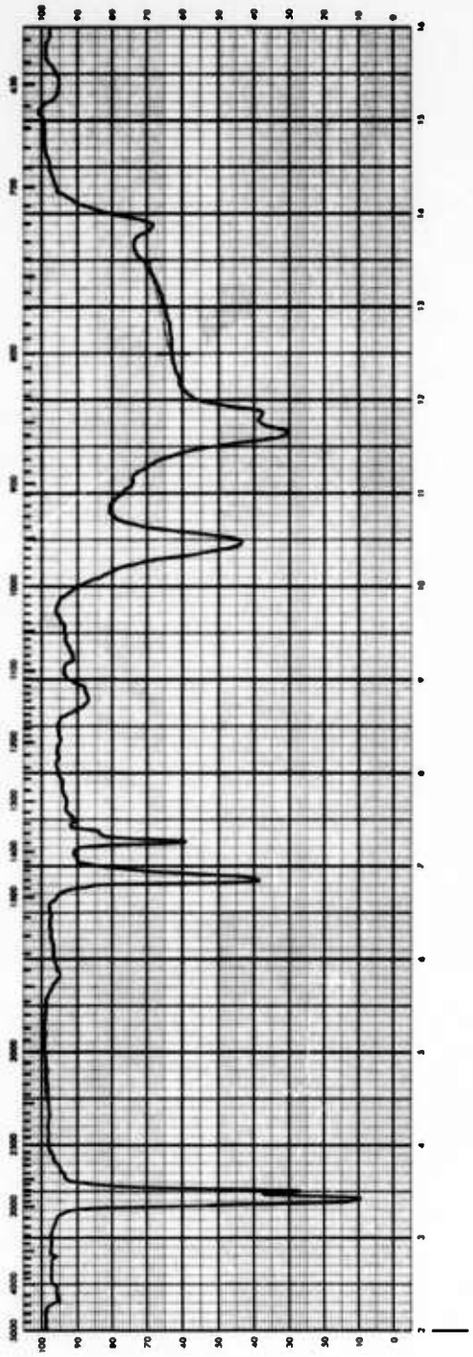


Fig. 5 Infrared Spectrum of Difluoraminooctane

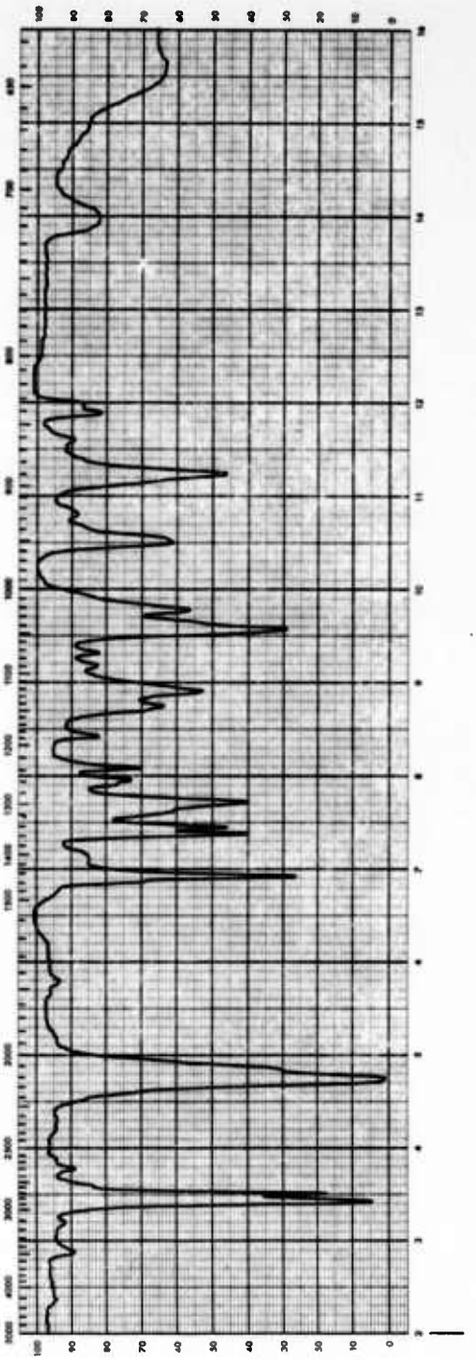


Fig. 6 Infrared Spectrum of β-(Difluoramino)butyric Acid

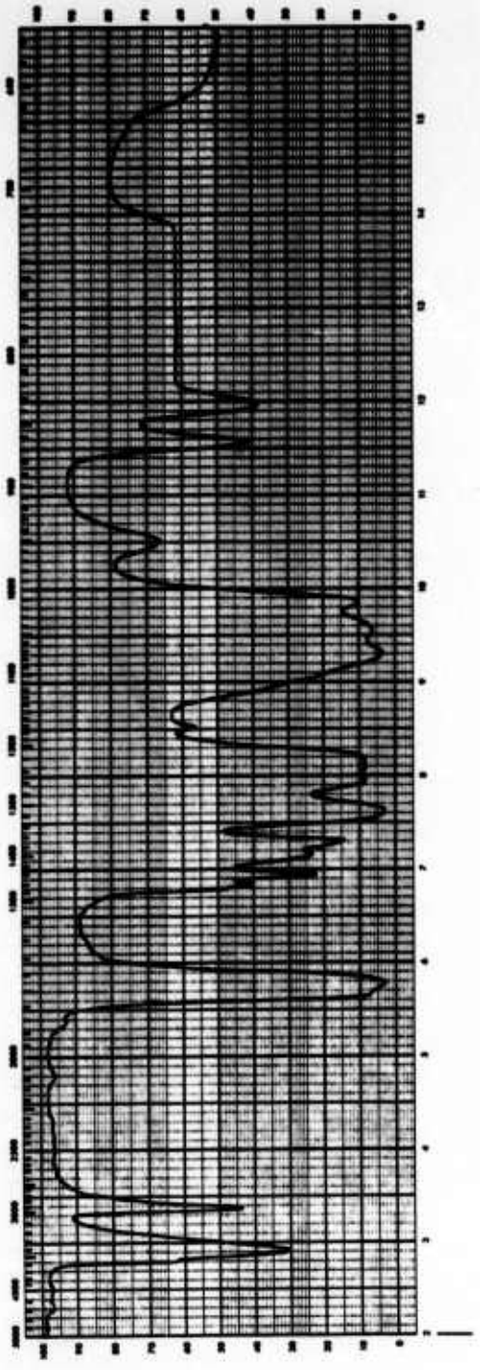


Fig. 7 Infrared Spectrum of Ethyl N-Fluoro-N-hydroxymethylcarbamate

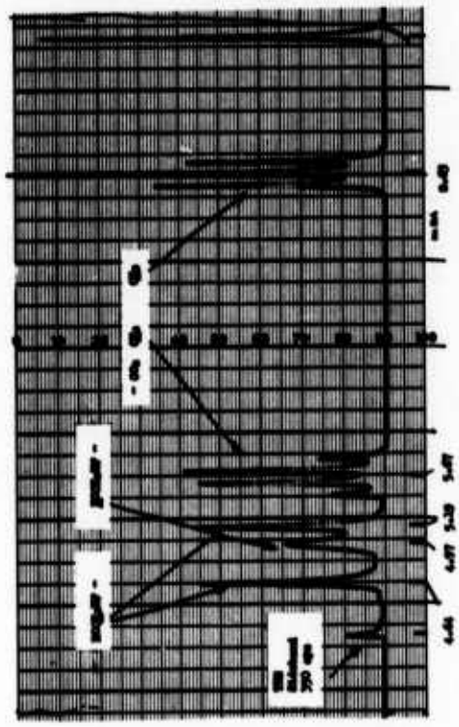


Fig. 8 Proton-NMR Spectrum of Ethyl N-Fluoro-N-hydroxymethylcarbamate

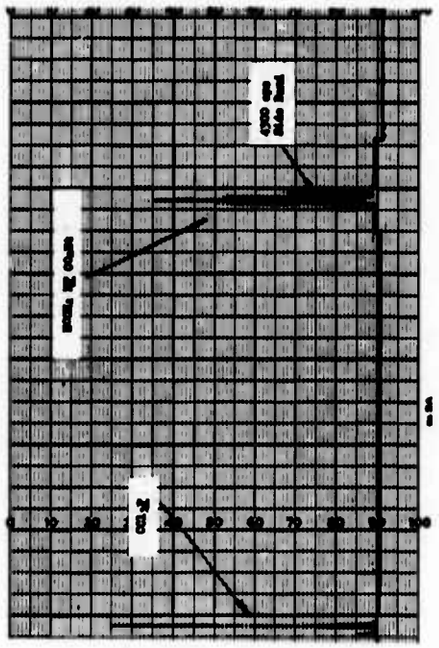


Fig. 9 $F^{19}$-NMR Spectrum of Ethyl N-Fluoro-N-hydroxymethylcarbamate

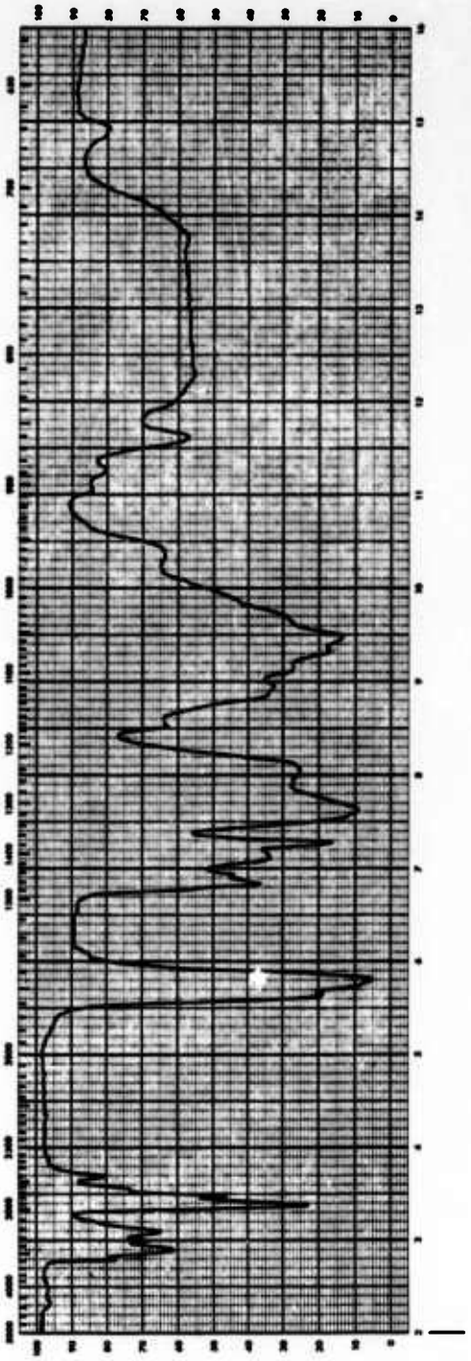


Fig. 10 Infrared Spectrum of Ethyl N-Fluoro-N-(1-hydroxy-n-butyl)carbamate

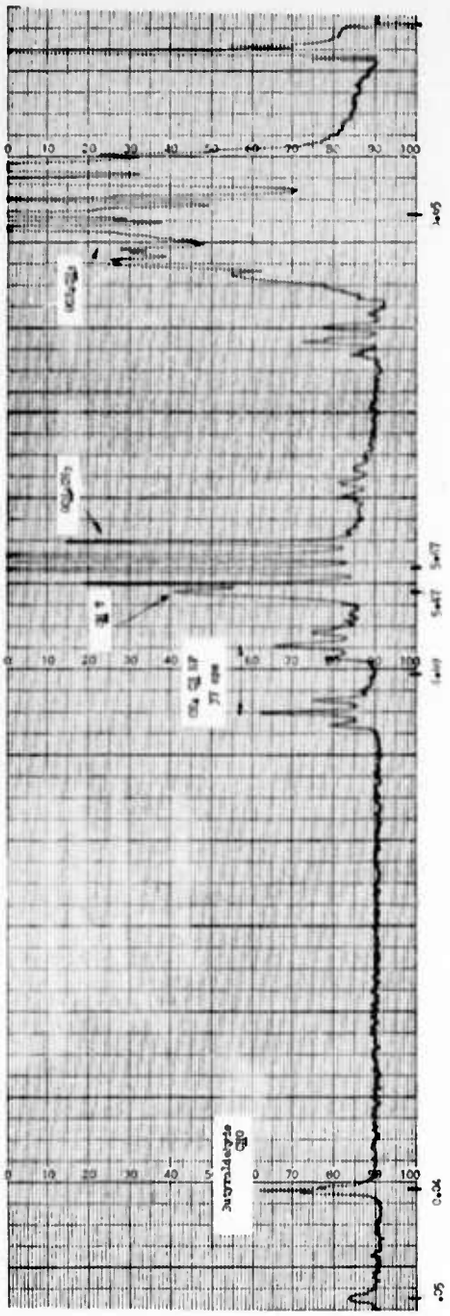


Fig. 11 Proton-NMR Spectrum of Ethyl N-Fluoro-N-(1-hydroxy-n-butyl)carbamate

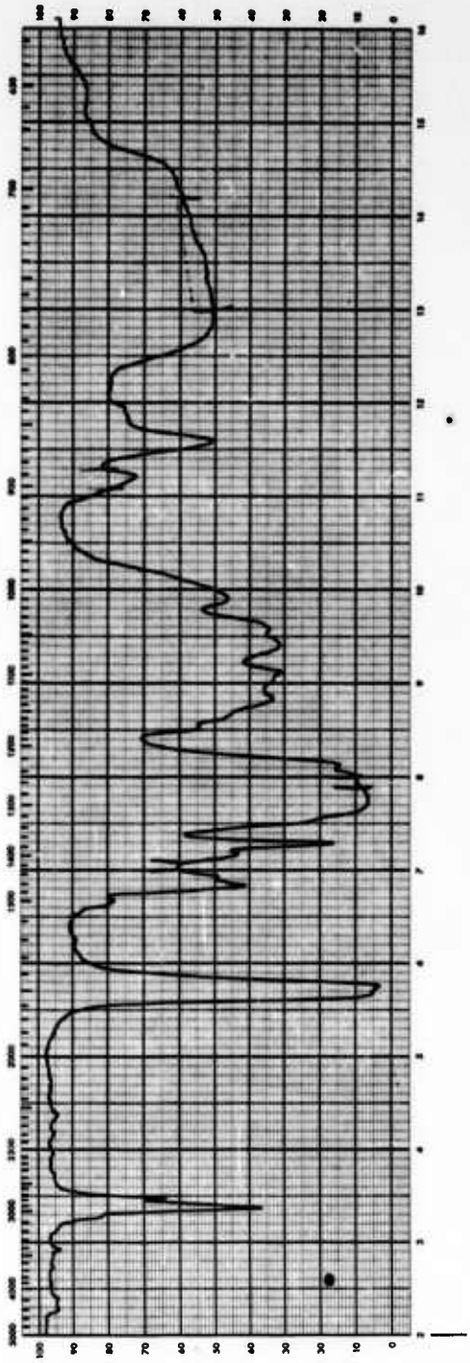


Fig. 12 Infrared Spectrum of N,N'-Difluoro-n-butylindinedicarbamate

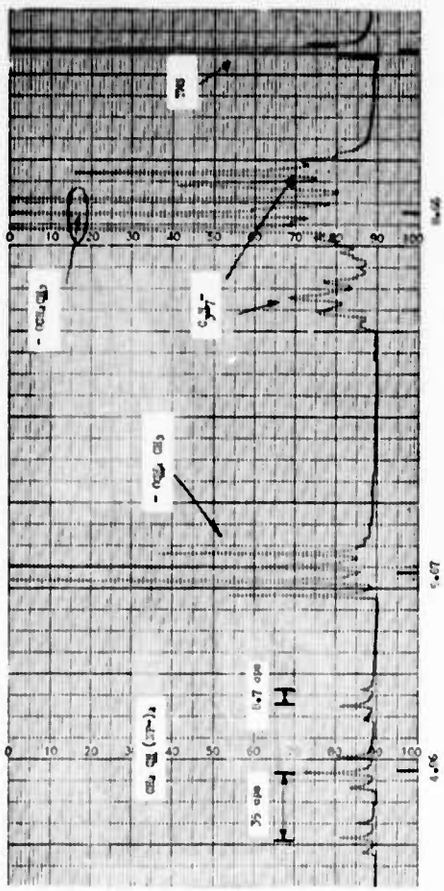


Fig. 13 Proton-NMR Spectrum of Diethyl N,N'-Difluoro-n-butylidinedicarbamate

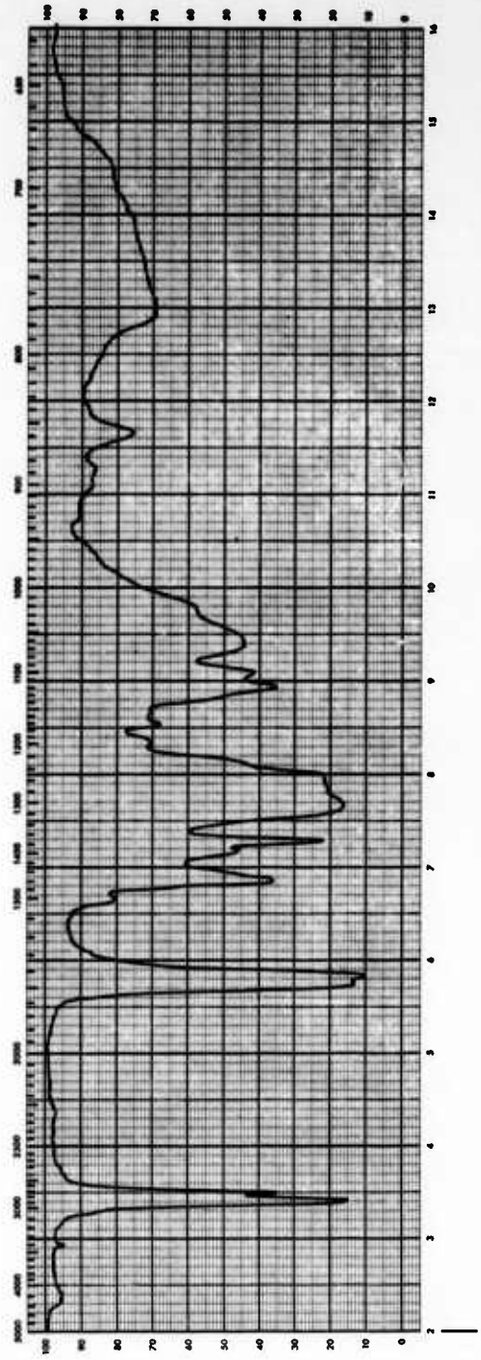
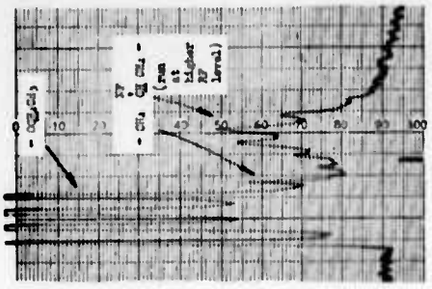


Fig. 14 Infrared Spectrum of Ethyl N-Fluoro-N-(2-octyl)carbamate



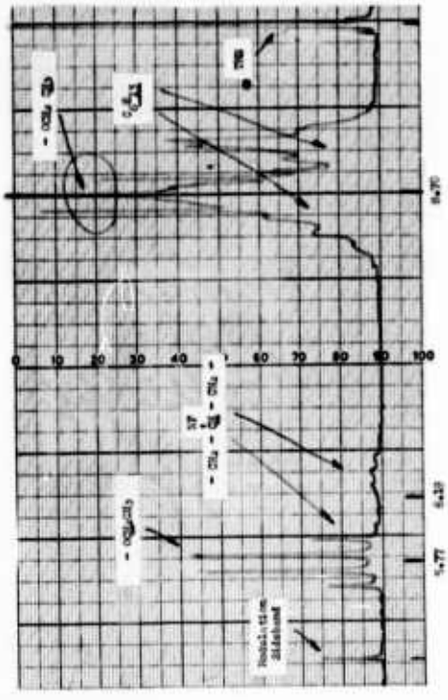


Fig. 15 Proton-NMR Spectra of Ethyl N-Fluoro-N-(2-octyl)carbamate

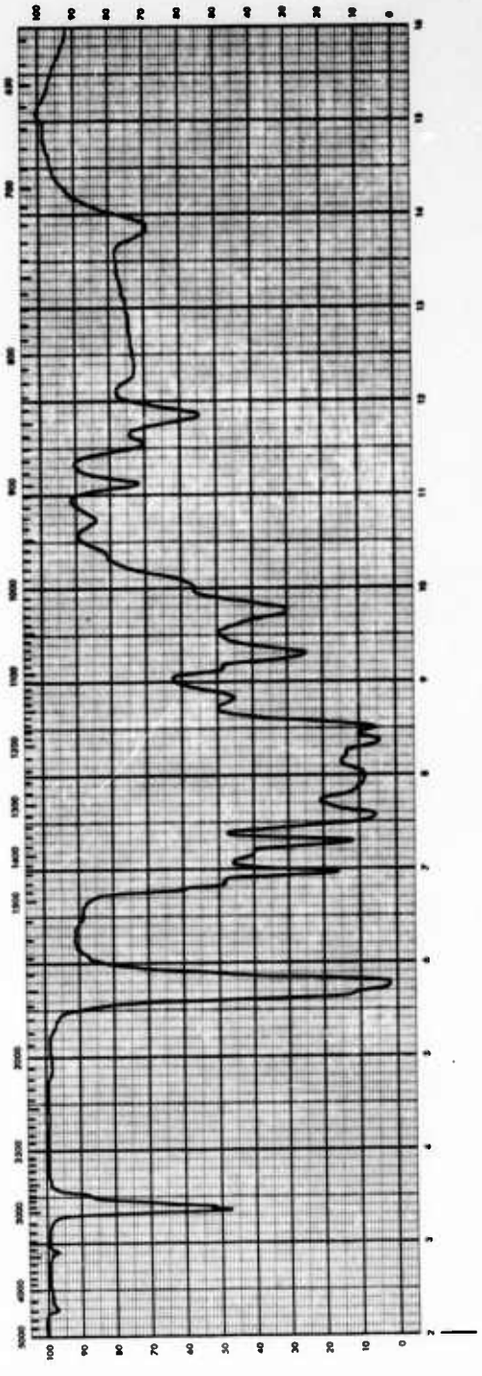
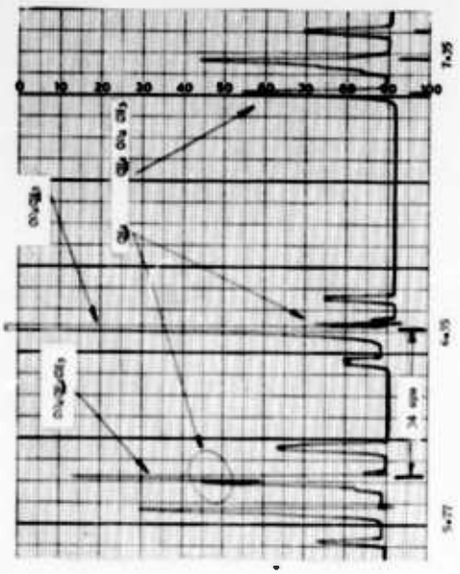


Fig. 16 Infrared Spectrum of Methyl N-Carbethoxy-N-fluoro-β-aminopropionate



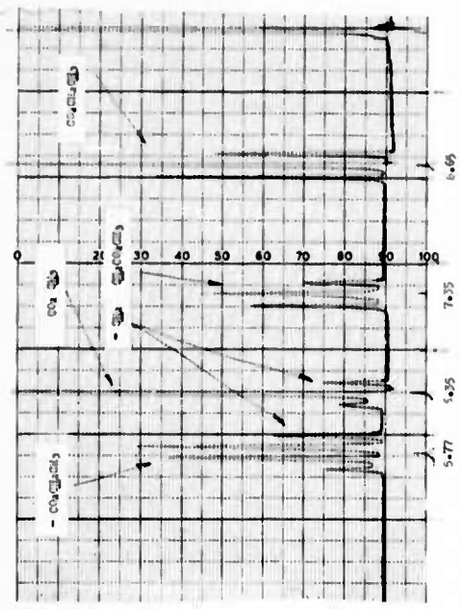


Fig. 17 Proton-NMR Spectra of Methyl N-Carbethoxy-N-fluoro-β-aminopropionate

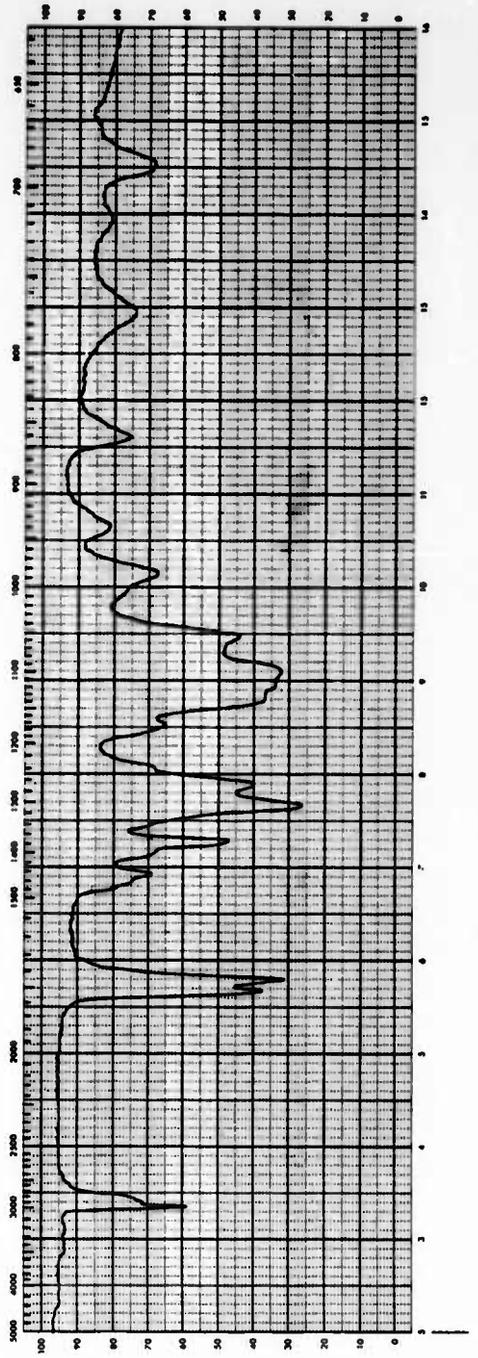


Fig. 18 Infrared Spectrum of Ethyl N-Fluoro-N-(α-ethoxy)ethylcarbamate

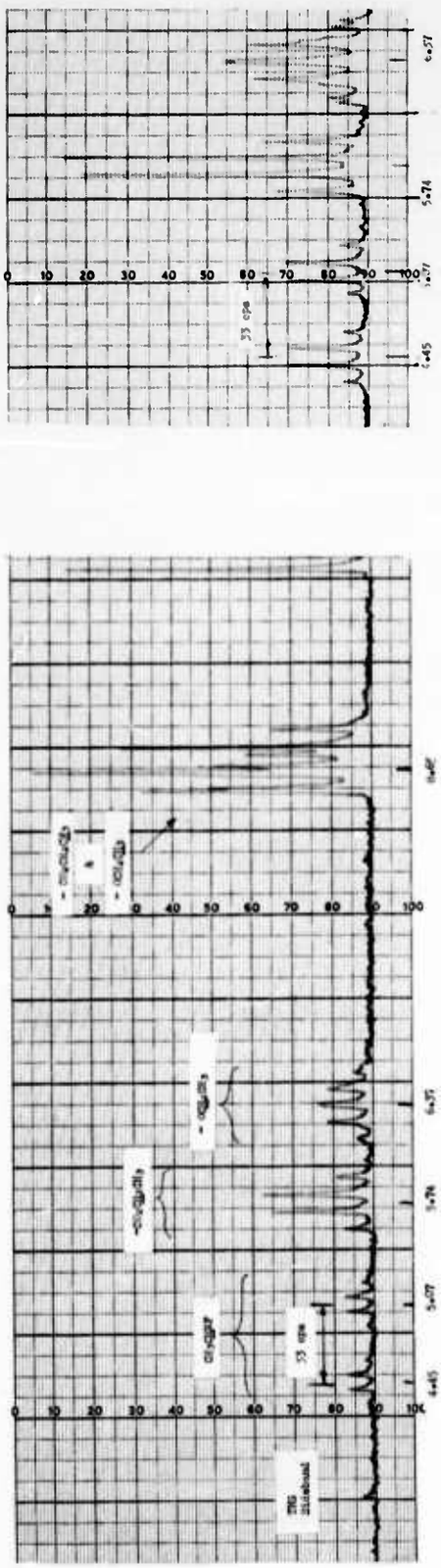


Fig. 19 Proton-NMR Spectra of Ethyl N-Fluoro-N-(α-ethoxy)carbamate

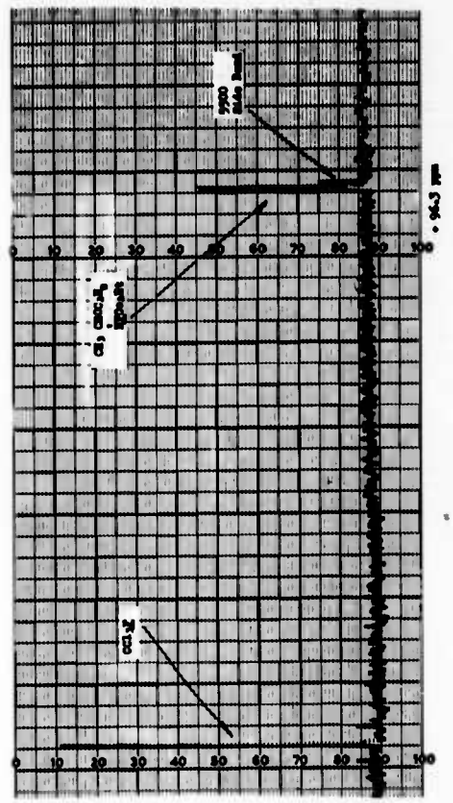


Fig. 20 F19-NMR Spectrum of Ethyl N-Fluoro-N-(α-ethoxy)ethylcarbamate

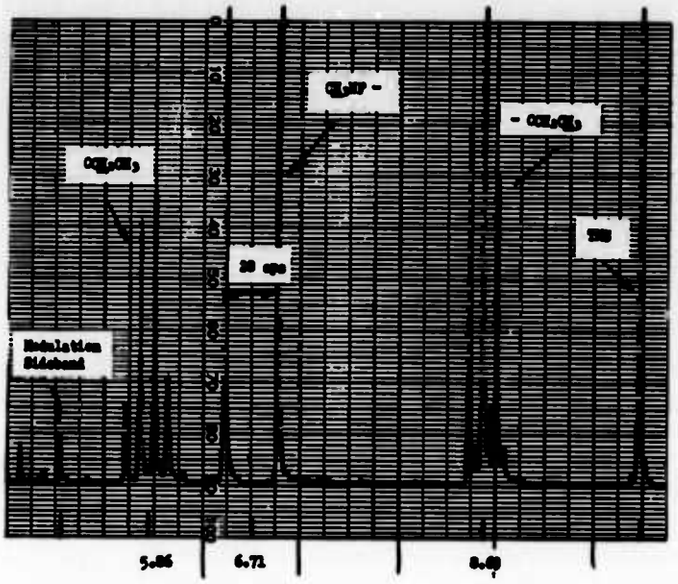



Fig. 21 Proton-NMR Spectrum of Ethyl N-Fluoro-N-methylcarbamate

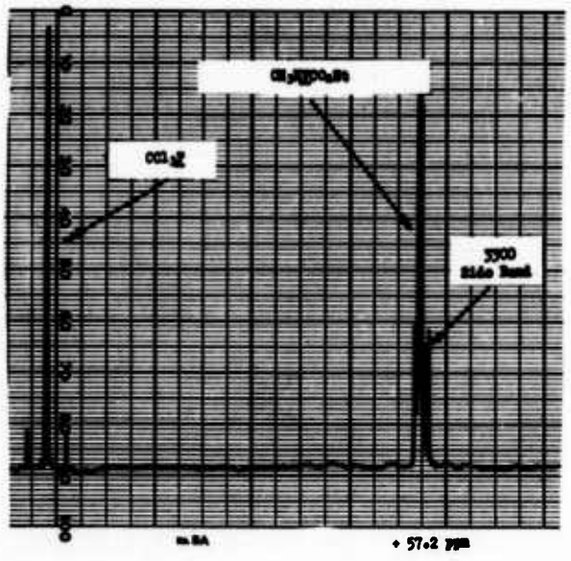


Fig. 22 $F^{19}$-NMR Spectrum of Ethyl N-Fluoro-N-methylcarbamate

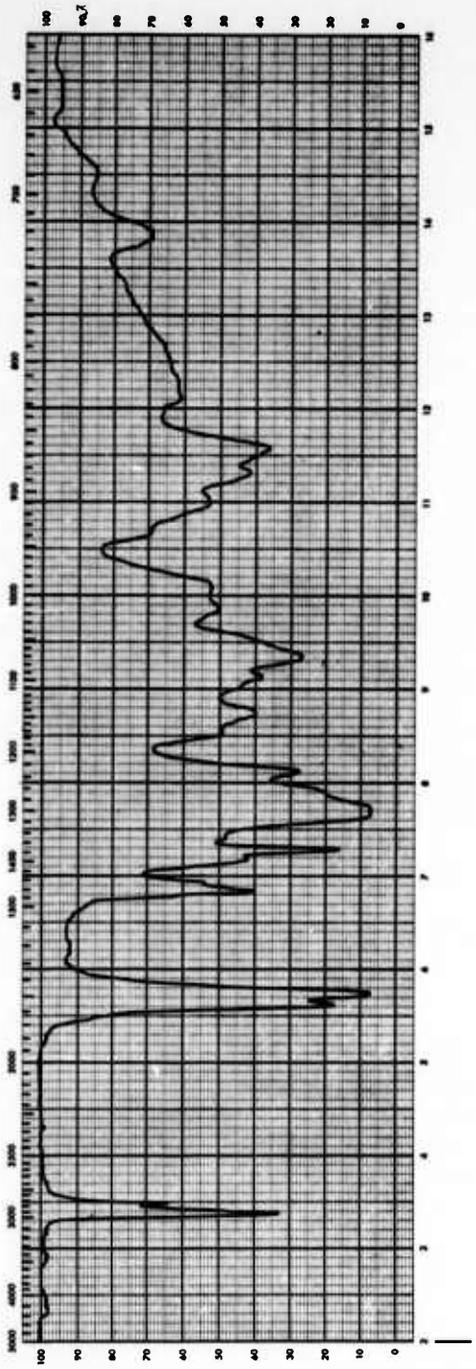


Fig. 23 Infrared Spectrum of Ethyl N-Fluoro-N-[1-(difluoramino)-n-butyl]carbamate

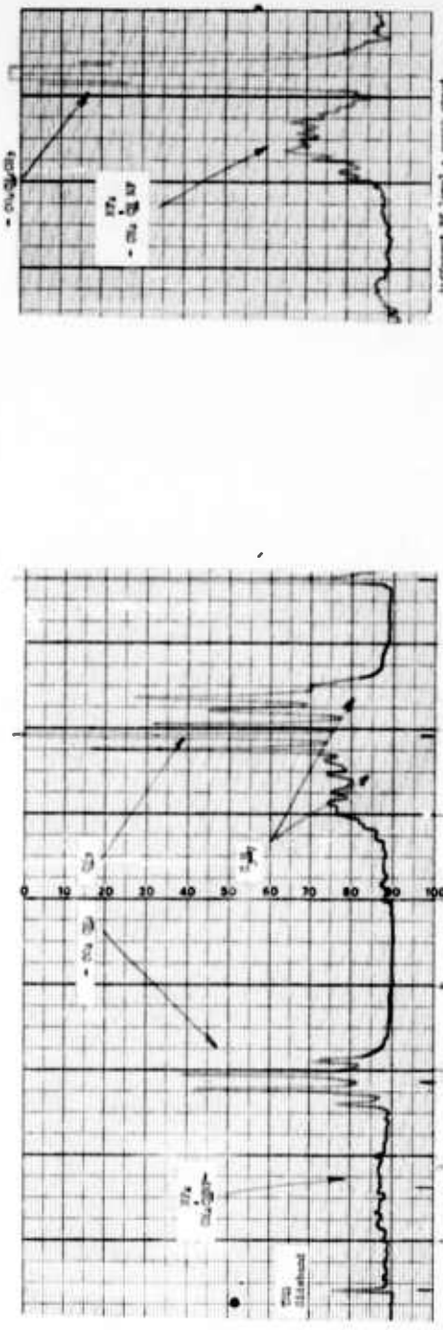


Fig. 24 Proton-NMR Spectra of Ethyl N-Fluoro-N-[1-(difluoramino)-n-butyl]carbamate

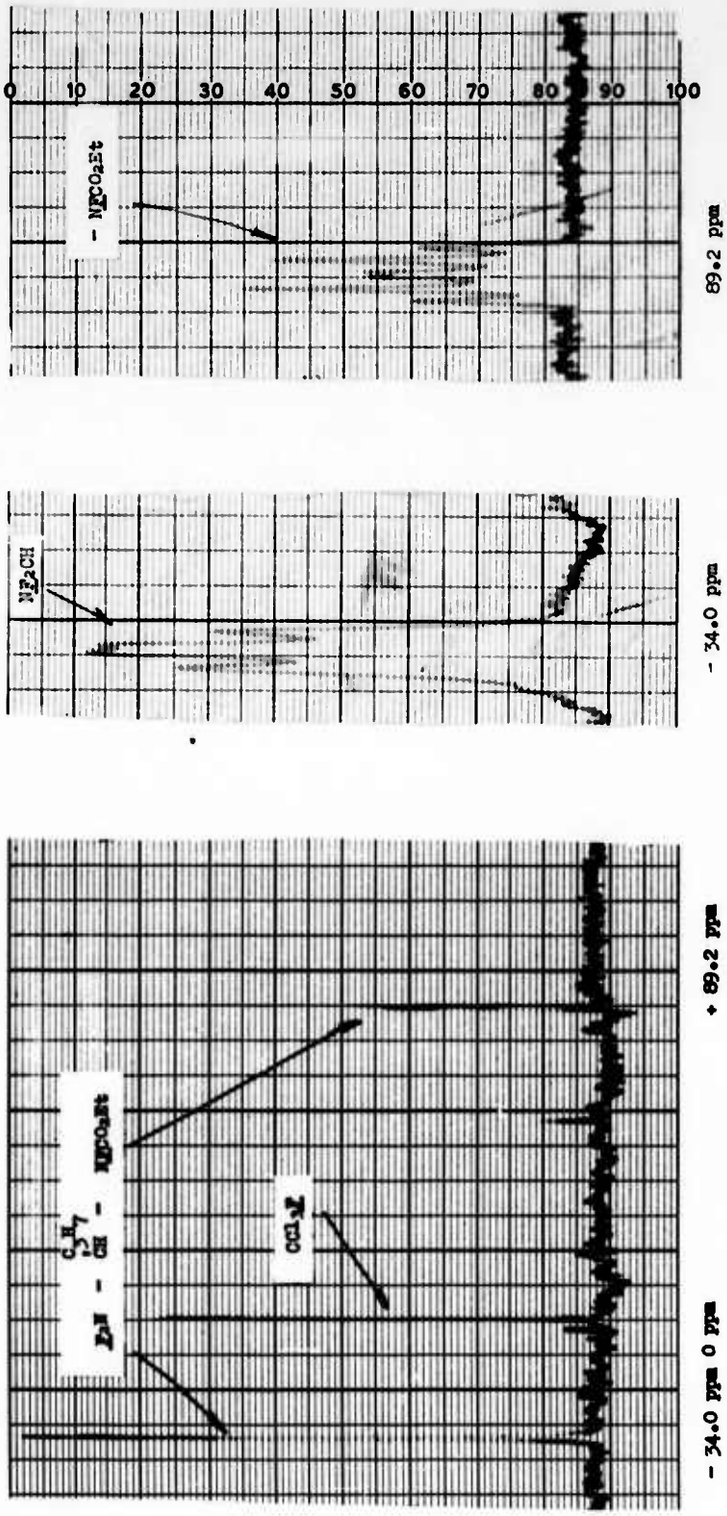



Fig. 25 $F^{19}$-NMR Spectra of Ethyl N-Fluoro-N-[1-(difluoramino)-n-butyl]carbamate

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